Theoretical Studies of Novel Organic Systems: Biradicals, Polyradicals, and Conducting Polymers

Thesis by

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to my parents

"The more progress the physical sciences make, the more they tend to enter the domain of mathematics, which is a kind of centre to which they all converge. We may even judge the degree of perfection to which a science has arrived by the facility with which it may be submitted to calculation."

A. Quetelet (1796–1874)

"Every attempt to employ mathematical methods in the study of chemical questions must be considered profoundly irrational and contrary to the spirit of chemistry. If mathematical analysis should ever hold a prominent place in chemistry—an aberration which is happily almost impossible—it would occasion a rapid and widespread degeneration of that science."

A. Compte (1798–1857)

Acknowledgements

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Abstracts

Chapter 1

Cyclobutanediyl has been studied in both its singlet and triplet states by ab initio electronic structure theory. The triplet, which is the ground state of the molecule, exists in both C_{2h} and C_{2v} forms, which interconvert via a C_s transition state. For the singlet, only a C_{2h} form is found. It passes, via a C_s transition state, onto the C_{2v} surface on which bicyclobutane is the only minimum. The ring-flipping (inversion) process in bicyclobutane includes the singlet biradical as an intermediate, and involves a novel, non-least motion pathway. Semiclassical periodic orbit theory indicates that the various minima on both the singlet and triplet surfaces can interconvert via quantum mechanical tunneling.

Chapter 2

The dimethylenepolycyclobutadienes (**n**) are the non-Kekulé analogues of the classical acenes. Application of a variety of theoretical methods reveals several novel features of such structures. Most interesting is the emergence of a parity rule. When n is even, **n** is predicted to be a singlet, with n disjoint NBMOs. When n is odd, theory predicts a triplet ground state with (n+1) NBMOs that are not fully disjoint.

Chapter 3

Bi(cyclobutadienyl) (**2**), the cyclobutadiene analogue of biphenyl, and its homologues tri- (**3**) and tetra(cyclobutadienyl) (**4**) have been studied using electronic structure theory. Ab initio calculations on **2** reveal that the central bond is a true double bond, and that the structure is best thought of as two allyl radicals plus an ethylene. The singlet and triplet states are essentially degenerate. Trimer **3** is two allyls plus a

dimethylenecyclobutanediyl, while **4** is two coplanar bi(cyclobutadienyl) units connected by a single bond. For both **3** and **4**, the quintet, triplet, and singlet states are essentially degenerate, indicating that they are tetraradicals. The infinite polymer, polycyclobutadiene, has been studied by HMO, EHCO, and VEH methods. Several geometries based on the structures of **3** and **4** have been studied, and the band structures are quite intriguing. A novel crossing between the valence and conduction bands produces a small band gap and a high density of states at the Fermi level.

Chapter 4

At the level of Hückel theory, polyfulvene has a HOCO-LUCO degeneracy much like that seen in polyacetylene. Higher levels of theory remove the degeneracy, but the band gap (E_g) is predicted to be significantly smaller than analogous structures such as polythiophene and polypyrrole at the fulvenoid geometry. An alternative geometry, which we have termed quinoid, is also conceivable for polyfulvene, and it is predicted to have a much larger E_g. The effects of benzannelation to produce analogues of polyisothianaphthene have been evaluated. We propose a new model for such structures based on conventional orbital mixing arguments. Several of the proposed structures have quite interesting properties, which suggest that they are excellent candidates for conducting polymers.

Chapter 5

Theoretical studies of polydimethylenecyclobutene and polydiisopropylidene-cyclobutene reveal that, because of steric crowding, they cannot achieve a planar, fully conjugated structure in either their undoped or doped states. Rather, the structure consists of essentially orthogonal hexatriene units. Such a structure is incompatible with conventional conduction mechanisms involving polarons and bipolarons.

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Chapter 1

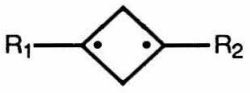
The Singlet and Triplet Potential Energy Surfaces of Cyclobutanediyl

Interest in organic biradicals initially stemmed from their presumed role as intermediates or transition states in a variety of thermal and photochemical processes.[1] Recently, direct observation of a variety of biradicals has become possible.[2] The field has matured to the extent that biradicals are now studied for their own inherently novel properties.

Two types of biradicals may be distinguished. "Delocalized" biradicals are structures in which the two unpaired electrons are part of the same conjugated π system. For such structures, the π-system topology exerts considerable influence on the electronic structure.[3] Most of the biradicals that have been observed to date belong to this class.[2] In "localized" biradicals, the two unpaired electrons are not in classical π conjugation with each other, although each may separately be part of a conjugated π system.

Direct observation of localized biradicals are rare. In 1975 Buchwalter and Closs reported the detection of the first localized hydrocarbon biradical, 1,3-cyclopentanediyl (**1-H**).[4] Almost ten years passed before a second example, 1,3-dimethyl-1,3-cyclobutanediyl (**2-Me**), was reported.[5a] A variety of cyclobutanediyls with different substituents (**2**) have now been observed.[5b] Very recently, the observation of 1,3-diphenyl-1,3-cyclopentanediyl (**1-Ph**) was reported.[6]

1-H : R=H
1-Ph : R=Ph



2-Me : $R_1=R_2=CH_3$
2-CD_3 : $R_1=R_2=CD_3$
2-Et : $R_1=R_2=CH_2CH_3$
2-Pr : $R_1=R_2=n\text{-}C_3H_7$
2-MP : $R_1=CH_3$, $R_2=Ph$
2-EV : $R_1=CH_2CH_3$, $R_2=CHCH_2$
2-Ph : $R_1=R_2=Ph$
2-Vin : $R_1=R_2=CHCH_2$
2-Vin-d_6 : $R_1=R_2=CDCD_2$

3

Theoretical studies of localized biradicals include investigations on the parent 1,3-biradical, trimethylene,[7] as well as on **1-H**.[8] Cyclobutanediyl (**3**, or **2-H**), the focus of the present work, has also been subjected to several previous theoretical studies.[9–14] In most cases these studies have been concerned with the inversion barrier of bicyclobutane, the closed-shell isomer of **3**.[9–11] As such, the focus was on the singlet state of **3**.

In the present work, the potential energy surface of both the singlet and triplet states of **3** are studied in detail, including the location and characterization of stationary points. Based on the potential energy surfaces, information about processes such as the inversion of bicyclobutane and the bond-forming reaction of triplet **3** are inferred.

Electronic Structure of Biradicals

From a molecular-orbital perspective, biradicals are characterized by the presence of two electrons in two nonbonding molecular orbitals (NBMOs) ϕ_a and ϕ_b (Figure 1). There are six possible configurations of the two electrons in the two NBMOs (Figure 2, a). Of these, the fifth and sixth are *not* eigenfunctions of the S^2 operator; however, their linear combinations are (Figure 2, b and c). ψ_3, ψ_4, and ψ_5 are the three components of a triplet state (S^2=2), while ψ_1, ψ_2, and ψ_6 form three distinct singlet states (S^2=0).

For "homosymmetric" biradicals,[15] of which **3** is an example, the two NBMOs ϕ_a and ϕ_b arise from linear combinations of two localized orbitals χ_l and χ_r (Eqs. 1 and 2); for **3**, these are essentially the p_z orbitals of the radical centers C_1 and C_3.

$$\phi_a = (2+2S_{lr})^{-1/2}(\chi_l+\chi_r) \quad (1)$$

$$\phi_b = (2-2S_{lr})^{-1/2}(\chi_l-\chi_r) \quad (2)$$

S_{lr} is the overlap matrix element between χ_l and χ_r. In cases where S_{lr} is small, ψ_1 and ψ_2 do *not* provide good descriptions of the singlet states. To see why, we expand ψ_1 and ψ_2 in terms of the localized orbitals χ_l and χ_r (Eqs. 3 and 4, assuming S_{lr}=0).

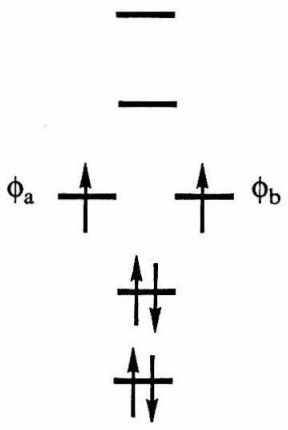
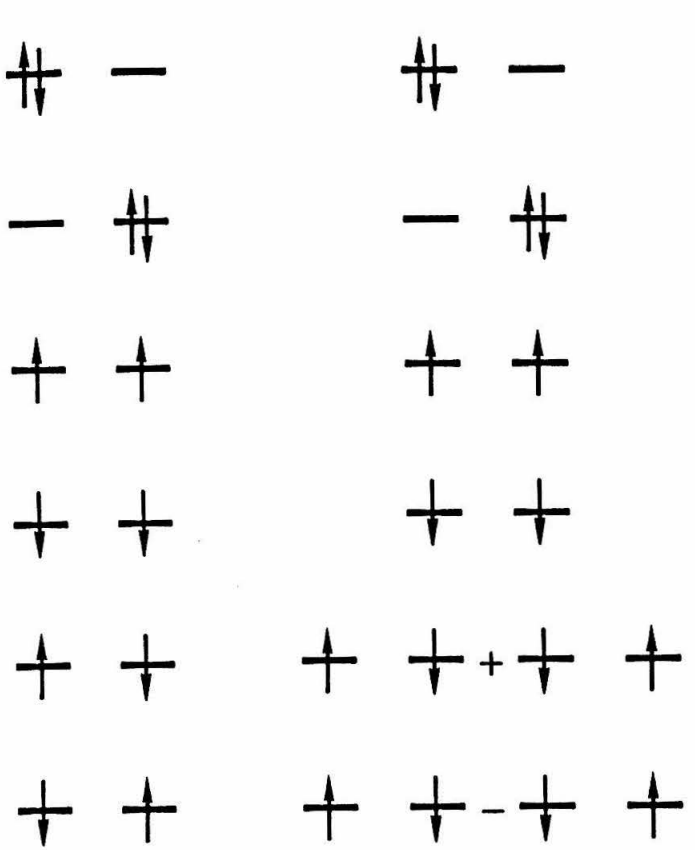


Figure 1. Molecular orbital representation of a biradical.



$$\Psi_1 = 2^{-1/2} \begin{vmatrix} \phi_a\alpha(1) & \phi_a\beta(1) \\ \phi_a\alpha(2) & \phi_a\beta(2) \end{vmatrix}$$

$$\Psi_2 = 2^{-1/2} \begin{vmatrix} \phi_b\alpha(1) & \phi_b\beta(1) \\ \phi_b\alpha(2) & \phi_b\beta(2) \end{vmatrix}$$

$$\Psi_3 = 2^{-1/2} \begin{vmatrix} \phi_a\alpha(1) & \phi_b\alpha(1) \\ \phi_a\alpha(2) & \phi_b\alpha(2) \end{vmatrix}$$

$$\Psi_4 = 2^{-1/2} \begin{vmatrix} \phi_a\beta(1) & \phi_b\beta(1) \\ \phi_a\beta(2) & \phi_b\beta(2) \end{vmatrix}$$

$$\Psi_5 = 2^{-1/2}\left\{2^{-1/2} \begin{vmatrix} \phi_a\alpha(1) & \phi_b\beta(1) \\ \phi_a\alpha(2) & \phi_b\beta(2) \end{vmatrix} + 2^{-1/2} \begin{vmatrix} \phi_a\beta(1) & \phi_b\alpha(1) \\ \phi_a\beta(2) & \phi_b\alpha(2) \end{vmatrix}\right\}$$

$$\Psi_6 = 2^{-1/2}\left\{2^{-1/2} \begin{vmatrix} \phi_a\alpha(1) & \phi_b\beta(1) \\ \phi_a\alpha(2) & \phi_b\beta(2) \end{vmatrix} - 2^{-1/2} \begin{vmatrix} \phi_a\beta(1) & \phi_b\alpha(1) \\ \phi_a\beta(2) & \phi_b\alpha(2) \end{vmatrix}\right\}$$

a b c

Figure 2. (a) Possible electronic configurations in a biradical. (b) Linear combinations that are eigenfunctions of the S^2 operator. (c) Determinant representations of the wave functions corresponding to the configurations in (b).

$$\psi_1=2^{-1}\left\{\left|\begin{matrix}\chi_l\alpha(1)&\chi_r\beta(1)\\ \chi_l\alpha(2)&\chi_r\beta(2)\end{matrix}\right|+\left|\begin{matrix}\chi_r\alpha(1)&\chi_l\beta(1)\\ \chi_r\alpha(2)&\chi_l\beta(2)\end{matrix}\right|+\left|\begin{matrix}\chi_l\alpha(1)&\chi_l\beta(1)\\ \chi_l\alpha(2)&\chi_l\beta(2)\end{matrix}\right|+\left|\begin{matrix}\chi_r\alpha(1)&\chi_r\beta(1)\\ \chi_r\alpha(2)&\chi_r\beta(2)\end{matrix}\right|\right\} \quad (3)$$

$$\psi_2=2^{-1}\left\{-\left|\begin{matrix}\chi_l\alpha(1)&\chi_r\beta(1)\\ \chi_l\alpha(2)&\chi_r\beta(2)\end{matrix}\right|-\left|\begin{matrix}\chi_r\alpha(1)&\chi_l\beta(1)\\ \chi_r\alpha(2)&\chi_l\beta(2)\end{matrix}\right|+\left|\begin{matrix}\chi_l\alpha(1)&\chi_l\beta(1)\\ \chi_l\alpha(2)&\chi_l\beta(2)\end{matrix}\right|+\left|\begin{matrix}\chi_r\alpha(1)&\chi_r\beta(1)\\ \chi_r\alpha(2)&\chi_r\beta(2)\end{matrix}\right|\right\} \quad (4)$$

The last two determinants in these wave functions correspond to situations where both electrons occupy the *same* localized orbital (χ_l or χ_r), giving rise to unfavorable coulomb repulsions. These "ionic" terms destabilize ψ_1 and ψ_2. However, the linear combination $(\psi_1-\psi_2)$ lacks these ionic terms (Eq. 5), whereas the other linear combination $(\psi_1+\psi_2)$ has *only* these ionic terms (Eq. 6).

$$2^{-1/2}(\psi_1-\psi_2) = 2^{-1/2}\left\{\left|\begin{matrix}\chi_l\alpha(1)&\chi_r\beta(1)\\ \chi_l\alpha(2)&\chi_r\beta(2)\end{matrix}\right|+\left|\begin{matrix}\chi_r\alpha(1)&\chi_l\beta(1)\\ \chi_r\alpha(2)&\chi_l\beta(2)\end{matrix}\right|\right\} \quad (5)$$

$$2^{-1/2}(\psi_1+\psi_2) = 2^{-1/2}\left\{\left|\begin{matrix}\chi_l\alpha(1)&\chi_l\beta(1)\\ \chi_l\alpha(2)&\chi_l\beta(2)\end{matrix}\right|+\left|\begin{matrix}\chi_r\alpha(1)&\chi_r\beta(1)\\ \chi_r\alpha(2)&\chi_r\beta(2)\end{matrix}\right|\right\} \quad (6)$$

The other singlet wave function, ψ_6, also consists only of ionic terms (Eq. 7), whereas the triplet wave functions (e.g., ψ_3) contain only covalent (i.e., noninonic) terms (Eq. 8).

$$\psi_6 = 2^{-1/2}\left\{\left|\begin{matrix}\chi_l\alpha(1)&\chi_l\beta(1)\\ \chi_l\alpha(2)&\chi_l\beta(2)\end{matrix}\right|-\left|\begin{matrix}\chi_r\alpha(1)&\chi_r\beta(1)\\ \chi_r\alpha(2)&\chi_r\beta(2)\end{matrix}\right|\right\} \quad (7)$$

$$\psi_3 = 2^{-1/2}\left\{\left|\begin{matrix}\chi_l\alpha(1)&\chi_r\beta(1)\\ \chi_l\alpha(2)&\chi_r\beta(2)\end{matrix}\right|-\left|\begin{matrix}\chi_r\alpha(1)&\chi_l\beta(1)\\ \chi_r\alpha(2)&\chi_l\beta(2)\end{matrix}\right|\right\} \quad (8)$$

To summarize, the biradical configurations give rise to four states: a triplet and three singlets. Two of the singlet states ($(\psi_1+\psi_2)$ and ψ_6, Eqs. 6 and 7) are dominated by ionic terms, making them quite high in energy. The low-lying, covalent singlet state is represented by a two-configuration wave function ($(\psi_1-\psi_2)$, Eq. 5), whereas the triplet state (or, more precisely, the $S_z=1$ or $S_z=-1$ component of the triplet state) is adequately described by a single configuration (e.g., Eq. 8).

Although it is safe to dismiss the *ionic* singlets as energetically high-lying states, it is not obvious whether the *covalent* singlet is above or below the triplet state. This depends on the magnitude of S_{lr}, or, equivalently, the energy difference between the NBMOs ϕ_a and ϕ_b.[14] When S_{lr} is close to zero, and ϕ_a and ϕ_b are very nearly degenerate, the two-electron exchange integral favors the triplet state, in accordance with Hund's rule. The triplet is usually the ground state in this situation. As S_{lr} becomes increasingly large and positive, and ϕ_a becomes increasingly stabilized at the expense of ϕ_b, the two-configuration wave function for the singlet (originally the expression in Eq. 5) becomes increasingly dominated by ψ_1. (If S_{lr} is large and *negative*, the roles of ϕ_a and ϕ_b are interchanged, as are those of ψ_1 and ψ_2.) This corresponds to the developing formation of a bond between the radical centers, and the singlet state is stabilized relative to the triplet. In the limit, of course, the NBMOs lose their nonbonding nature and become a bonding and antibonding pair of MOs. The singlet becomes a closed-shell state, which can be described by a single configuration ψ_1 (or ψ_2).

The overlap matrix element S_{lr}, which as we have seen is crucial in determining the singlet–triplet energy difference, contains contributions from both direct (through-space) and indirect (through-bond) interactions. The importance of these interactions has been investigated.[14]

Computational Methods

Our interest is in investigating the lowest singlet and triplet states of **3**. The considerations presented in the previous section dictate the necessary levels of theory: The triplet state is adequately described by an RHF (restricted Hartree-Fock) wave function,[16] whereas the singlet requires a TCSCF (two-configuration-self-consistent-field) wave function, or an equivalent GVB (generalized valence bond) wave function.[17] All the

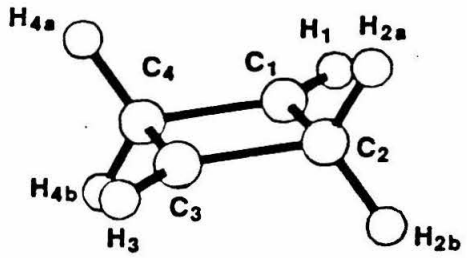
calculations described in this chapter were performed using the Gaussian 86 program package.[18]

Geometry optimizations were performed using the 3-21G basis set.[19] In most cases these are followed by single-point calculations using the 6-31G* basis set.[20] For stationary points, the geometries were completely optimized, subject only to molecular symmetry constraints. The stationary points were characterized as local minima, transition states, or higher-order saddle points, by performing frequency calculations to determine the number of imaginary frequencies (zero, one, or more than one, respectively). For points along a reaction pathway, one geometric parameter corresponding to the reaction coordinate was fixed, and all remaining coordinates were optimized within molecular symmetry constraints.

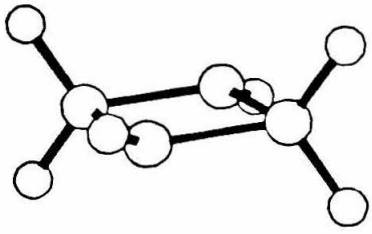
The Triplet Potential Energy Surface

We initially optimized the geometry of the triplet state of **3** within D_{2h} symmetry constraints. However, the frequency calculation on the optimized structure (**3a**, Figure 3) revealed the presence of two imaginary frequencies, which correspond to the symmetric and antisymmetric out-of-plane bending motions (symmetries b_{1u} and b_{3g}) of H_1 and H_3. (Our choice of coordinate system places the cyclobutane ring in the xy-plane, with the CH_2 groups along the x-axis.) These distortions strongly indicate the existence of local minima having C_{2v} and C_{2h} symmetries, respectively.

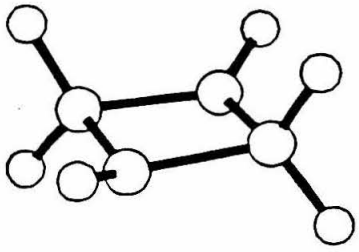
Optimizations with C_{2h} and C_{2v} symmetry constraints led to stationary points (**3b** and **3c**, respectively), which were characterized as local minima (i.e. no imaginary frequencies). In addition, we located the transition state (C_s symmetry) for the interconversion between these two minima (**3d**). The structures and energies of these stationary points are shown in Figure 3, and detailed geometrical parameters are given in Table I.



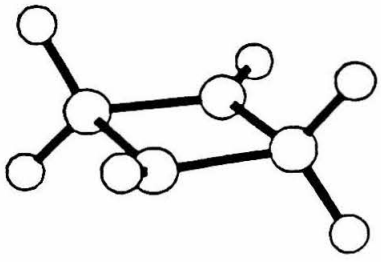
3a
D_{2h} double maximum
Energy (3-21G) = 0.61
Energy (6-31G*) = 1.20



3b
C_{2h} minimum
Energy (3-21G) = 0.0
Energy (6-31G*) = 0.0



3c
C_{2v} minimum
Energy (3-21G) = 0.15
Energy (6-31G*) = 0.21



3d
C_s transition state
Energy (3-21G) = 0.31
Energy (6-31G*) = 0.58

Figure 3. Structures and relative energies of stationary points on the triplet potential energy surface. Energies in kcal/mol relative to **3b** (total energy =−153.962410 a.u. (3-21G) or −154.827167 a.u. (6-31G*)).

Table I. Structures of stationary points on the triplet potential energy surface.[a,b]

Structure	**3a**	**3b**	**3c**	**3d**
C_1C_3	2.1017	2.1108	2.1191	2.1112
C_1C_2=C_1C_4	1.5354	1.5406	1.5403	1.5344
C_3C_2=C_3C_4	1.5354	1.5406	1.5403	1.5419
C_1H_1	1.0672	1.0706	1.0704	1.0674
C_3H_3	1.0672	1.0706	1.0704	1.0706
C_2H_{2a}=C_4H_{4a}	1.0856	1.0847	1.0857	1.0857
C_2H_{2b}=C_4H_{4b}	1.0856	1.0847	1.0837	1.0846
$C_1C_3H_3$[c]	180.0	157.56	160.82	158.24
$C_3C_1H_1$[c]	180.0	202.44	160.82	179.17
XC_2H_{2a}=XC_4H_{4a}[d]	125.48	125.42	124.60	125.06
XC_2H_{2b}=XC_4H_{4b}[d]	125.48	125.42	126.17	125.82
C_2XC_4 (flap angle)[d,e]	180.0	180.0	185.48	183.37

[a]See Figure 3, particularly **3a**. [b]Bond lengths in angstroms, angles in degrees. [c]These angles are measured above the ring plane as drawn in Figure 3. [d]X is a point along the C_1C_3 vector such that C_1X and C_2X are perpendicular. [e]This angle is measured below the ring plane as drawn in Figure 3.

Contrary to what was previously assumed,[14] these calculations indicate that triplet **3** is not planar. In both minima, H_1 and H_3 are substantially removed (by an angle of about 20°) from the plane of the ring. We might also point out that these geometries were optimized with the 3-21G basis set, which is known to underestimate the extent of pyramidalization.[21] This is reflected in the greater energy differences between the planar and nonplanar forms in the 6-31G* calculations. The relative stabilities among the structures remain the same.

While the hydrogens show substantial deviations from planarity, the cyclobutane ring itself remains essentially planar. In **3b**, the ring is necessarily planar by symmetry. In **3c**, the deviation from planarity is only about 5°. Interestingly, the ring puckers towards the *same* face of the ring as H_1 and H_3. In both structures, the planes containing the CH_2 groups remain essentially perpendicular to the plane of the ring. This is constrained by symmetry in **3c**; in **3b** the deviation from perpendicularity is only 0.3°.

The transition state structure (**3d**) can be seen to be intermediate in structure between **3b** and **3c** (Figure 3, Table I). One methine hydrogen (H_1) is essentially in the plane of the ring, and the single imaginary frequency in this structure corresponds to the bending motion of this hydrogen.

The experimental studies on derivatives of **3** (i.e., **2**) included characterization of these structures by electron paramagnetic resonance (EPR) spectroscopy.[5] These studies provided much information on the molecular and electronic structure of the triplet states of these biradicals, in that the zero-field splitting parameters were quantitatively correlated to the spin distributions in the molecules. In addition, the EPR spectra of some structures displayed interpretable hyperfine coupling, which showed a single, large hyperfine coupling constant with the ring methylene hydrogens.

Figure 4 shows contour plots of the singly occupied molecular orbitals for both **3b** and **3c** in the plane containing $H_1C_1C_3H_3$. From these plots we estimate that the

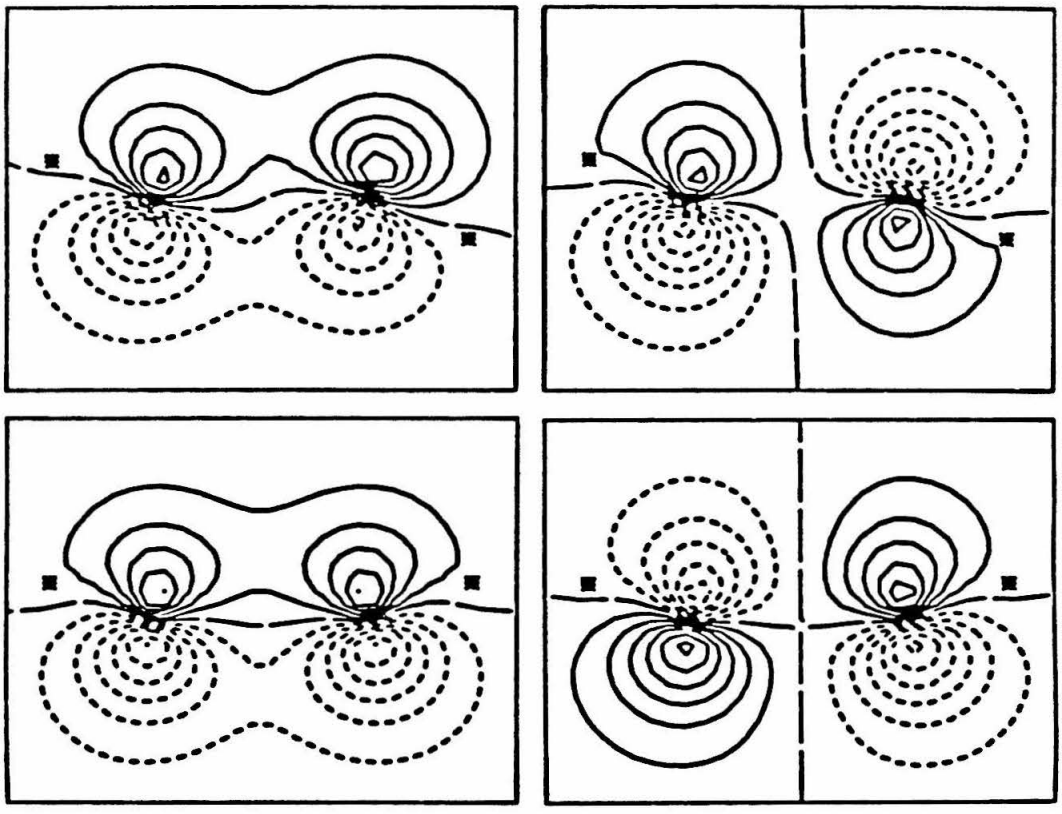


Figure 4. Contour plots of the singly occupied molecular orbitals in **3b** (top) and **3c** (bottom) in the $H_1C_1C_3H_3$ plane.

orbitals containing the radical electrons are tilted from the *z*-axis by about 12° in **3b** and by about 10° in **3c**. The orientation of these orbitals are important in determining the value of the EPR β-hyperfine coupling constant (a_H^β). For *planar* radical centers, these are given by the relation[22]

$$a_H^\beta = A + \rho C \cos^2\theta, \qquad (9)$$

where ρ is the electron density at the radical center; A and C are constants with typical values of 0–5 and 40–45 G, respectively; and θ is the dihedral angle between the axis of the *p* orbital on the α-carbon and the β C–H bond. For the pyramidalized radical centers of interest here, this equation is perhaps best considered as a semiquantitative guideline.

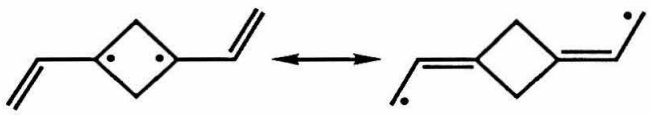
In **3c** we expect two hyperfine couplings, because the CH_2 protons are not equivalent. The two values for θ are 21° and 30°. Using A=1.2 G, C=42.5G, and ρ=1 in Eq. 9,[5] we obtain values of 33 and 38 G for a_H^β. The difference of 5 G is comparable to a typical linewidth in a triplet spectrum.

In **3b** all the CH_2 protons are symmetry-equivalent, and we expect a single hyperfine coupling constant. However, there are still two different values of θ, 18° and 35°. Attempts to apply Eq. 9 to **3b** produce values of 30 and 40 G for a_H^β, which are in acceptable agreement with the value of 32 G observed in the spectra of **2-CD$_3$**.[5] We note that simulation of this experimental spectrum required an unusually large linewidth, which may be caused by a mixture of C_{2h} and C_{2v} forms, or, perhaps, tunneling (see below).

The question remains whether the substituted cyclobutanediyls (**2**) also adopt a C_{2h}-like structure. We have performed single-point calculations (using the 3-21G basis set) on dimethylcyclobutanediyl (**2-Me**), using the geometry optimized for **3** for the ring and the optimized geometry of the *t*-butyl radical for the methyl groups.[23] The relative energy ordering of **2-Me** structures derived from **3a–3d** remains unchanged. The C_{2h}-like structure is of the lowest energy, followed by the C_{2v}-like structure (0.23 kcal/mol

higher), then the C_s-like structure (1.08 kcal/mol), and the D_{2h}-like structure has the highest energy (2.28 kcal/mol). While these values would certainly change upon optimization, the results indicate that there are no major changes expected in the cyclobutanediyl structure upon substitution with a localized substituent.

We do expect changes when the substituent is a delocalizing group. For example, in divinylcyclobutanediyl (**2-Vin**), delocalization would provide a substantial driving force towards planarity. We assume that this delocalization energy is sufficient to overcome the small intrinsic preference for nonplanarity in the cyclobutanediyl framework. We have not been able to explore this question, however, since calculations on **2-Vin** would be quite a significant undertaking, requiring full correlation of at least six π electrons.[24]



2-Vin

The Singlet Potential Energy Surface. Inversion Process of Bicyclobutane

Singlet **3** has generally been regarded as a transition state or an intermediate in the inversion process of bicyclobutane (**4**).

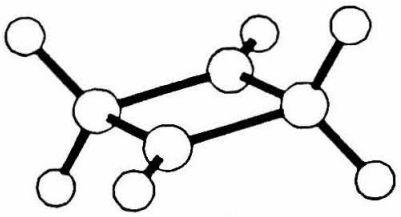
4 **3** **4**

Collins and co-workers have reported a single imaginary frequency for the D_{2h} structure, indicating that it is a transition state.[11] However, their calculations were done at the RHF level, a wholly inadequate level of theory for such a molecule, in that it fails to treat the biradical nature of the structure adequately. The inversion barrier they obtained (82.5 kcal/mol) was unrealistically large, further illustrating the failure of the RHF

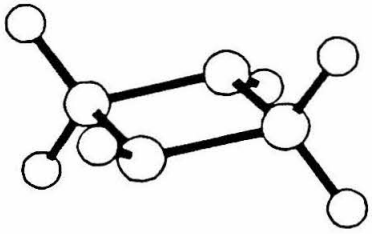
method for this type of system. Inclusion of some level of electron correlation via MP3 and CI methods did not substantially alter these results. In contrast, the barriers obtained by Schleyer and co-workers (using TCSCF/3-21G)[10] and by Gassman and co-workers (using TCSCF/PRDDO)[9] were much more realistic, but somewhat too small (29.1 and 23.2 kcal/mol, respectively). While the actual barrier height has not been determined experimentally, it is known that **4** undergoes a thermal ring-opening process to give butadiene with an activation energy of 40.6 kcal/mol, rather than undergoing inversion.[25] Thus, the inversion barrier has to be significantly higher than 40.6 kcal/mol, and thermochemical estimates suggest a value in the vicinity of 47 kcal/mol.[26]

In addition to obtaining the barrier height, Gassman and co-workers also traced the inversion pathway. They did this by using the flap angle of **4** as the reaction coordinate. What they found was that the inversion process does not follow a least-motion pathway. Surprisingly, the bridgehead hydrogens initially move *inward* as the flap angle increased.[27] At a flap angle of about 150°, the hydrogens reverse their direction of motion and move outward towards planarity. Gassman also found a shallow local minimum on the inversion pathway, corresponding to a structure with a planar cyclobutane ring, but having H_1 and H_3 out of plane (C_{2v} symmetry). The structure of this minimum was not optimized, and it was postulated that the D_{2h} structure was the transition state between this shallow minimum and its inverted couterpart.

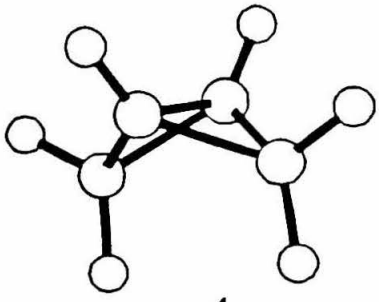
In our own work we began by optimizing the D_{2h} structure (**3e**, Figure 5, Table II). This structure is, of course, identical to Schleyer's, which was obtained at an identical level of theory, and is qualitatively similar to Gassman's. Collins' structure has an unreasonably short C_1–C_3 distance (1.86 Å), which is no doubt a consequence of using RHF theory. Our frequency calculation on **3e** resulted in two imaginary frequencies, as was found for the triplet state. Optimization within C_{2h} symmetry resulted



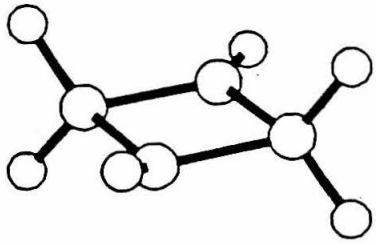
3e
D_{2h} double maximum
Energy (3-21G) = 0.94
Energy (6-31G*) = 1.49



3f
C_{2h} minimum
Energy (3-21G) = 0.0
Energy (6-31G*) = 0.0



4
C_{2v} minimum (bicyclobutane)
Energy (3-21G) = –28.19
Energy (6-31G*) = –38.42



3g
C_s transition state
Energy (3-21G) = 0.66
Energy (6-31G*) = 1.02

Figure 5. Structures and relative energies of stationary points on the singlet potential energy surface. Energies in kcal/mol relative to **3f** (total energy =–153.960117 a.u. (3-21G) or –154.824840 a.u. (6-31G*)).

Table II. Structures of stationary points on the singlet potential energy surface.[a,b]

Structure	**3e**	**3f**	**3g**	**4**
C_1C_3	2.1030	2.1509	2.1178	1.5296
C_1C_2=C_1C_4	1.5403	1.5463	1.5385	1.5134
C_3C_2=C_3C_4	1.5403	1.5463	1.5467	1.5134
C_1H_1	1.0674	1.0733	1.0676	1.0616
C_3H_3	1.0674	1.0733	1.0707	1.0616
C_2H_{2a}=C_4H_{4a}	1.0842	1.0831	1.0842	1.0745
C_2H_{2b}=C_4H_{4b}	1.0842	1.0831	1.0836	1.0760
$C_1C_3H_3$[c]	180.0	147.05	156.64	133.56
$C_3C_1H_1$[c]	180.0	212.95	184.34	133.56
XC_2H_{2a}=XC_4H_{4a}[d]	125.27	125.16	125.08	121.48
XC_2H_{2b}=XC_4H_{4b}[d]	125.27	125.16	125.44	123.71
C_2XC_4 (flap angle)[d,e]	180.0	180.0	181.73	119.98

[a]See Figure 5, and also Figure 3, particularly **3a**. [b]Bond lengths in angstroms, angles in degrees. [c]These angles are measured above the ring plane as drawn in Figure 5. [d]X is a point along the C_1C_3 vector such that C_1X and C_2X are perpendicular. [e]This angle is measured below the ring plane as drawn in Figure 5.

in a local minimum (**3f**), but we found no minimum with C_{2v} symmetry other than bicyclobutane. In addition, we found a transition state with C_s symmetry (**3g**).

Our calculations thus indicate that singlet **3** lies in a minimum. This singlet biradical has C_{2h} symmetry, like the lowest energy structure of the corresponding triplet, and it lies in a reasonably deep well (1 kcal/mol below the C_s form at the 6-31G* level). In contrast, the parent 1,3-biradical trimethylene (**5**) does not exhibit a (computational) minimum on the singlet surface.[7] It closes without activation to cyclopropane. Apparently, ring strain is enough to induce a true well on the singlet surface of a localized 1,3-biradical.

5

Inspection of the transition state (**3g**) indicates that its single imaginary frequency corresponds to the motion of H_1. This is expected for a transition structure between a C_{2v} (**4**) form and a C_{2h} form (**3f**). We have attempted to calculate intermediate points in this reaction pathway. Starting from bicyclobutane (**4**), gradual deformation of one of the bridgehead hydrogens does not lead to the transition state structure. In fact, the flap angle decreases (from 120° to 117°) and the C_1–C_3 bond shortens (1.530 to 1.523 Å) as the hydrogen angle is deformed from 133.6° in **4** to 160° (Table III). Instead, we find a reaction pathway that does result in the breaking of the C_1–C_3 bond (and formation of a biradical) by opening up the flap angle of the ring (i.e., the same pathway proposed by Gassman and co-workers).[9] This C_{2v} path is shown in Table IV. Unlike Gassman, however, we do not find a minimum on this reaction pathway. Instead, the energy keeps increasing as we deform the flap angle beyond 180°. We do observe a relatively flat surface in the neighborhood of 180°.

On the other hand, when we start with the C_s transition state **3g** and follow the mode corresponding to the imaginary frequency (i.e., the motion of H_1), we appear to be

Table III. Structures obtained by deformation of the $C_3C_1H_1$ angle from bicyclobutane.[a]

$C_3C_1H_1$ angle	134[b]	140	150	160
C_1C_3	1.5296	1.5212	1.5183	1.5233
C_1C_2	1.5134	1.5144	1.5196	1.5270
C_3C_2	1.5134	1.5150	1.5136	1.5104
$C_1C_3H_3$	133.56	134.73	135.80	136.31
flap angle	119.98	118.89	117.77	117.08
Energy (3-21G)	0	0.38	2.67	7.12
Energy (6-31G*)	0	0.65	3.18	7.65

[a]Bond lengths in angstroms, angles in degrees, energies in kcal/mol relative to bicyclobutane. [b]Structure corresponding to bicyclobutane.

Table IV. Structures obtained by deformation of the flap angle of bicyclobutane.[a]

Flap angle	120[b]	130	140	150	160	170	175	180	185	190	200	210
C_1C_3	1.5296	1.6187	1.7948	1.8726	1.9614	2.0845	2.1143	2.1235	2.1246	2.1238	2.1173	2.0962
C_1C_2	1.5134	1.5088	1.5232	1.5318	1.5420	1.5512	1.5505	1.5480	1.5463	1.5457	1.5464	1.5481
$C_1C_3H_3$	133.56	123.42	110.32	110.83	115.90	130.92	141.07	149.95	156.19	159.95	164.80	170.38
Energy (3-21G)	0	2.01	5.07	11.02	19.30	26.15	27.59	28.08	28.22	28.41	29.45	31.76
Energy (6-31G*)	0	[c]	[c]	[c]	[c]	34.57	37.00	37.96	38.31	[c]	[c]	[c]

[a]Bond lengths in angstroms, angles in degrees, energies in kcal/mol relative to bicyclobutane. [b]Structure corresponding to bicyclobutane. [c]6-31G* energies not calculated.

Table V. Structures obtained by deformation of the $C_3C_1H_1$ angle from **3g**.[a]

$C_3C_1H_1$ angle	184[b]	175	160
C_1C_3	2.1178	2.1153	2.1210
C_1C_2	1.5385	1.5390	1.5440
C_3C_2	1.5467	1.5469	1.5468
$C_1C_3H_3$	156.64	158.37	155.71
flap angle	181.73	184.59	183.62
Energy (3-21G)	28.85	28.70	28.25
Energy (6-31G*)	39.45	[c]	38.40

[a]Bond lengths in angstroms, angles in degrees, energies in kcal/mol relative to bicyclobutane. [b]Structure corresponding to **3g**. [c]6-31G* energy not calculated.

Table VI. Comparison between near-coincident structures (**3h**) from Tables IV and V.[a]

	From Table IV	From Table V
C_1C_3	2.1246	2.1210
$C_1C_2=C_1C_4$	1.5463	1.5440
$C_3C_2=C_3C_4$	1.5463	1.5468
C_1H_1	1.0716	1.0706
C_3H_3	1.0716	1.0717
$C_2H_{2a}=C_4H_{4a}$	1.0845	1.0844
$C_2H_{2b}=C_4H_{4b}$	1.0825	1.0825
$C_1C_3H_3$	156.19	155.71
$C_3C_1H_1$	156.19	160.0[c]
$XC_2H_{2a}=XC_4H_{4a}$[b]	124.64	124.88
$XC_2H_{2b}=XC_4C_{4b}$[b]	125.85	125.63
C_2XC_4 (flap angle)[b]	185.0[c]	183.62

[a]Bond lengths in angstroms, angles in degrees. [b]X is a point along the C_1C_3 vector such that C_1X and C_2X are perpendicular. [c]These coordinates were constrained in the optimizations.

approaching a structure of C_{2v} symmetry (Table V). The structures represented in the last column of Table V and the 185° column in Table IV are, in fact, quite similar, as shown in more detail in Table VI. It appears, then, that the reaction pathway obtained by following the reaction coordinate from the transition state (**3g**) intersects the one obtained by following the flap angle from **4**, the intersection point (**3h**) being the structure shown in Table VI.

Based on these observations, we propose the following pathway in the inversion of **4**. Initially, the reaction coordinate is well represented by the flap angle of **4**. This is similar to the reaction pathway proposed by Gassman, and the "wrong way" motion of the bridgehead hydrogens is also observed here (Table IV). This pathway leads to a "plateau" at a flap angle of about 180° (**3h**). At a flap angle near 185°, one of the hydrogens starts to move faster than the other. This leads to a C_s transition state (**3g**) and ultimately to a C_{2h} intermediate (**3f**). From this point on, the other hydrogen's motion takes over, taking the molecule past a second C_s transition state (equivalent to the first) and ending back on a C_{2v} plateau. From this point on, it is a steep downhill path to inverted **4**. This is a lower energy pathway than the one obtained by staying within C_{2v} symmetry, following the flap angle. The reaction pathway is shown in Figure 6.

We note that this pathway is similar in spirit to the one proposed by Gassman and co-workers,[9] in that it involves a change in the molecular internal coordinate that corresponds to the "reaction coordinate". The main difference is that in Gassman's pathway C_{2v} symmetry is maintained throughout the process, whereas we have discovered a lower energy pathway if this constraint is relaxed. We also point out that the current pathway is somewhat more fully characterized, in that we have located a true transition state based on its single imaginary frequency, and the involvement of the D_{2h} structure is ruled out on the basis of its having two imaginary frequencies.

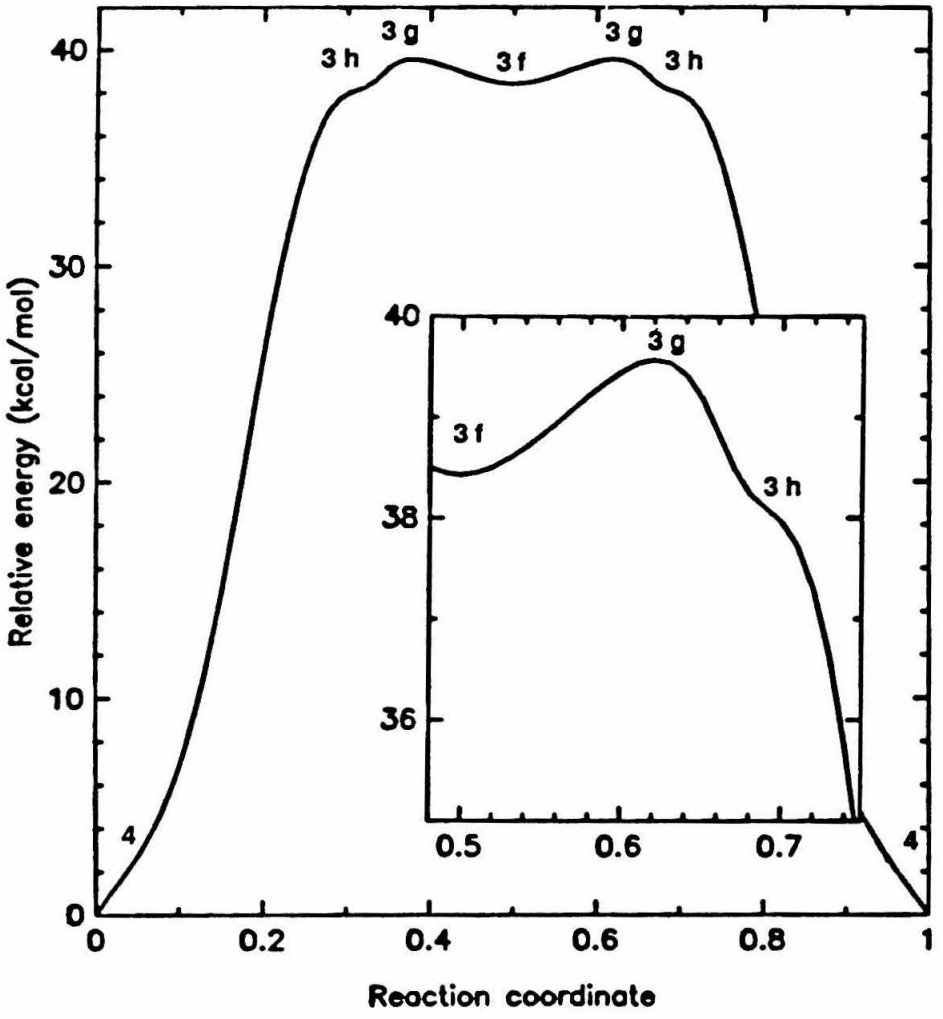


Figure 6. Reaction pathway in the singlet inversion of bicyclobutane. Inset is an expansion of the region near the transition state. Energies are at the 6-31G* level relative to bicyclobutane.

The structures and energies we obtained for **4** and **3e** are identical to those obtained by Schleyer and co-workers,[10] since both were done at the TCSCF/3-21G level. By invoking a lower energy transition state, the inversion barrier is 28.85 kcal/mol at the 3-21G level. As pointed out above, this value is too small. Considerable improvement is achieved when the calculation is done at the 6-31G* level. The inversion barrier is now 39.44 kcal/mol. This is much closer to the expected value, and we presume that the results might be improved further if the geometries were optimized at the 6-31G* level.

This is the correct inversion pathway *at this level of theory*. Some of the energy differences, though, are quite small—e.g., **3e** vs. **3g** is less than 0.5 kcal/mol. The same is true of the geometry differences between consecutive structures along the path. Higher levels of theory could reverse the relative ordering of some structures, and, of course, the "true" (i.e., experimental) inversion path could also differ from that of Figure 6. We believe, however, that the general form of this path is correct.

As in the triplet case, we expect the presence of delocalizing substituents to alter the structure and energy of the biradical significantly. In particular, 1,3-diphenyl-2,4-dicarbomethoxybicyclobutane undergoes inversion with an activation barrier of 26 kcal/mol.[28] This can be rationalized by a stabilization of the transition state due to the delocalizing phenyl groups. The presence of delocalizing groups would also tend to planarize the biradical structures.

Singlet–Triplet Gaps

In Table VII we show the singlet–triplet energy differences for **3** at various geometries corresponding to minima and transition states on the triplet and singlet surfaces. For all these points, the triplet is always below the singlet in energy. The energy difference between the lowest triplet (**3b**) and the lowest singlet (**3f**) structures is 1.46 kcal/mol at the 6-31G* level. It has been shown previously that this substantial triplet

Table VII. Vertical singlet–triplet gaps (kcal/mol).

Structure	S–T gap (3-21G)	S–T gap (6-31G*)
3b	1.80	1.78
3c	1.44	1.14
3d	1.77	1.56
3f	0.66	0.65
3g	1.79	1.64

preference in **3** is a consequence of a fortuitous balance between direct (through-space) and indirect (through-bond) overlaps of the two radical centers.[14] Both interactions are strong, but they are opposite in sign, so the net effect is that they almost completely cancel each other. The radical centers in **3** essentially have no overlap. However, the exchange repulsions between the two centers are still quite substantial, and so a triplet preference is the result.

Tunneling in Cyclobutanediyls

The potential energy surfaces of **3** show several minima separated by fairly low barriers. The structures of these minima differ from each other mainly in the positions of H_1 and H_3; thus, conversion from one minimum to another would involve mainly the motions of these hydrogens. Given the small mass of the moving particle and the low energy barriers involved, it seems feasible that quantum mechanical tunneling could play a major role.

Another motivation to study tunneling in this system arises from studies of the matrix isolation kinetics of **2**.[29] Structures with delocalizing substituents (**2-Vin**, **2-EV**, and **2-Ph**) exhibit normal (i.e., Arrhenius) behavior, while large deviations from such behavior are observed in the fully localized biradicals **2-Me** and **2-Et**. The latter result also suggests that quantum mechanical tunneling may be a major factor in the decay process of simple cyclobutanediyls.

The existence of C_{2h} (**3b**, **3f**) and C_{2v} (**3c**) minima instead of the more symmetrical D_{2h} structure is reminiscent of a Jahn-Teller distortion. The tunneling dynamics of Jahn-Teller distorted molecules have been studied using semiclassical periodic orbit theory.[30,31] We have therefore used this method to calculate tunneling rates in **3**.

A qualitative picture of tunneling between two potential energy minima is shown in Figure 7. For simplicity, we assume that the two wells are identical in shape. When the two are isolated (Fig. 7, top), each well has its own set of vibrational energy levels (e.g., E_l and E_r) and the corresponding set of vibrational wave functions (e.g., ψ_l and ψ_r). Each wave function has its maximum probability density within the well. When the two wells are brought together (Fig. 7, bottom), two related things happen. First, a splitting (ΔE) of the vibrational energy levels occurs. Second, the wave functions from the two wells interact with each other, resulting in new wave functions (e.g., $\psi_l+\psi_r$) which have probability density maxima in *both* wells. Therefore, a particle represented by this wave function may be found with equal probability in either of the two wells. In the time-dependent representation, the particle moves back and forth periodically between the two wells. This is true even when the energy level of the particle is below the top of the barrier. This, of course, is tunneling.

It can be shown that the rate at which a particle tunnels from one minimum to the other is given by the relation[31a,32]

$$k = \frac{2\Delta E}{h}, \tag{10}$$

where ΔE is the splitting of the energy level of the particle and h is Planck's constant.

Using semiclassical periodic orbit theory, Miller has derived the expression for the splitting of a given energy level E_0 to be[30a]

$$\Delta E = \frac{e^{-\theta}}{\pi n'(E_0)}, \tag{11}$$

where $n'(E_0)$ is formally dn/dE evaluated at $E=E_0$. In the harmonic oscillator approximation,

$$E_n = (n + \tfrac{1}{2})h\nu, \tag{12}$$

and therefore,

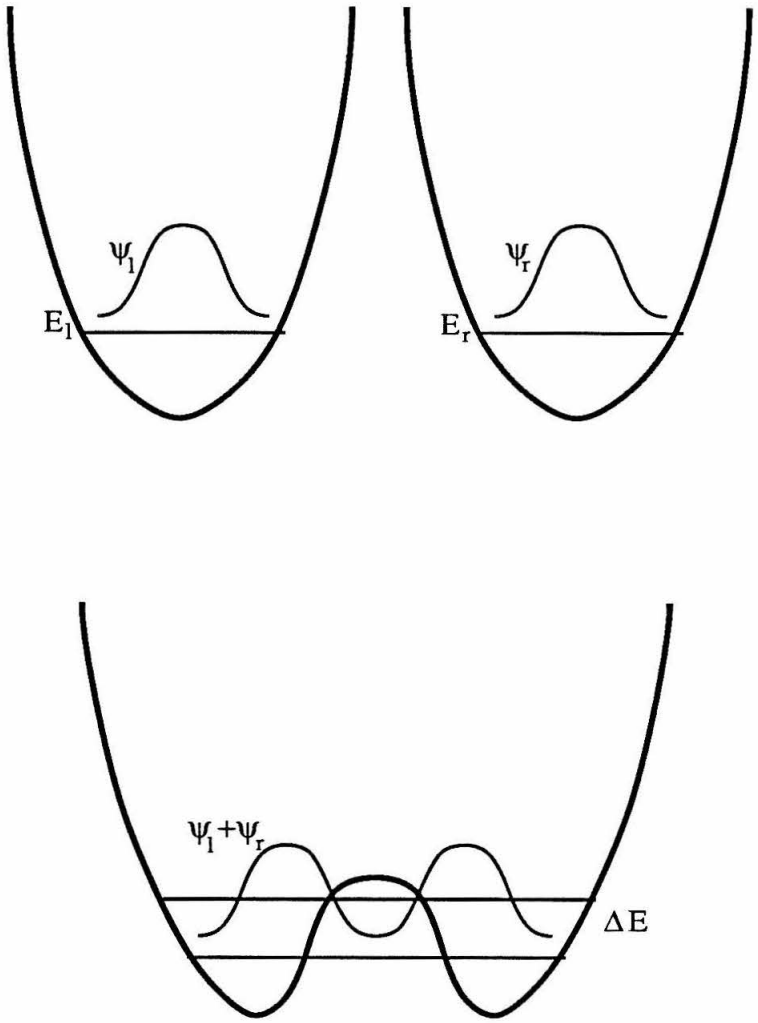


Figure 7. Schematic representation of tunneling between two potential minima. Top: Two isolated potential wells, showing the lowest vibrational energy level and a representation of the corresponding vibrational wave function in each well. Bottom: Two potential wells separated by a barrier, showing the splitting of the lowest vibrational energy level. Also shown is a representation of the vibrational wave function corresponding to the lower energy level. For clarity, the wave function corresponding to the higher level is not shown.

$$n'(E) = \frac{dn}{dE} = (h\nu)^{-1}; \tag{13}$$

i.e. n'(E) is independent of the energy level. Substituting into Eq. 11 we obtain

$$\Delta E = \frac{h\nu e^{-\theta}}{\pi}, \tag{14}$$

which is the usual and most useful form of this expression.[30b,31a]

The quantity θ in Eqs. 11 and 14 is the "barrier penetration integral",[30a,32]

$$\theta = \frac{2\pi}{h}\int_{x_1}^{x_2}\sqrt{2m[V(x)-E]}\,dx, \tag{15}$$

which is a measure of the permeability of the barrier. In this expression, m is the mass of the tunneling particle, E its energy, x_1 and x_2 are positions along the reaction coordinate where V(x)=E. In our calculations we used the Eckart barrier,[32] defined by

$$V(x) = \frac{4V_0 e^{x/b}}{(1+e^{x/b})^2}, \tag{16}$$

where V_0 is the barrier height and b is a parameter related to the barrier width. For this barrier,

$$\theta = \frac{4\pi^2}{h} b\sqrt{2m}(V_0^{1/2}-E^{1/2}), \tag{17}$$

as given by Bell.[32]

Eq. 17 may be restated in the following way. The imaginary frequency at the top of the barrier is given by

$$\nu_i = \frac{1}{2\pi}\sqrt{\frac{(d^2V/dx^2)_{x=0}}{m}}, \tag{18}$$

where $(d^2V/dx^2)_{x=0}$ is the "force constant" (the second derivative of the potential energy) evaluated at the top of the barrier; i.e.,

$$(d^2V/dx^2)_{x=0} = -\frac{V_0}{2b^2}. \tag{19}$$

Thus, Eq. 18 becomes

$$\nu_i = \frac{i}{2\pi b}\sqrt{\frac{V_0}{2m}}. \tag{20}$$

Substituting into Eq.17, we obtain[30b,31a]

$$\theta = \frac{2\pi}{h(\nu_i/i)}(V_0 - \sqrt{V_0}E). \tag{21}$$

The advantage of using this particular formulation of θ is that it avoids the concepts of "tunneling mass" and "barrier width", which for complex reaction pathways are often ambigous. Instead, they are replaced by an imaginary frequency ν_i, which can be easily obtained from a frequency calculation on the transition state corresponding to the structure at the top of the barrier.

Calculations of tunneling rates utilize Equations 10, 14, and 21. In applying these equations to actual systems, several further considerations should be taken into account.[30b,31a] First, the actual system is a multidimensional system (having many normal modes), whereas the model accounts for only one dimension. Therefore, one normal mode must be chosen as the mode corresponding to the reaction coordinate. This is usually not a problem, and the frequency of this mode is ν in Eq. 14. Second, the existence of other normal modes modifies the potential wells. This is done by modifying the barrier height, taking into account the zero-point energies of these coordinates,[30b,31a]

$$V_{eff} = V_0 + \tfrac{1}{2}\sum_k (h\nu_k^{\ddagger} - h\nu_k), \tag{22}$$

where the summation is over all the normal modes *except* the mode corresponding to the reaction coordinate; $\nu_k^{\ddagger}$ and ν_k are the frequencies of these modes in the transition state (i.e., the top of the barrier) and the minima (i.e., the bottom of the wells), respectively. In the actual calculation, V_0 in Eq. 21 is replaced by V_{eff}.

Finally, E in Eq. 21 is the energy of the tunneling particle; in the real system this energy corresponds to the vibrational energy levels of the normal mode corresponding to

the reaction coordinate. Each level has its own tunneling rate, and the overall rate is obtained by a Boltzmann-weighted summation over all the energy levels below the barrier. (For levels above the barrier, the reaction does not involve tunneling.) However, in our calculations on **3**, there is only one level below the barrier, so the summation is not necessary.

The discussion above is applicable only to tunneling in symmetrical systems, i.e., where the two potential energy wells have identical depth and width. For asymmetrical systems in which the reactant and product wells are not identical, several modifications are necessary. First of all, ΔE now corresponds to energy level *shifts* instead of splitting. As derived by Miller,[30a] this is a higher order term in θ,

$$\Delta E = \frac{e^{-2\theta}}{[2\pi n_1'(E_1)][2\pi n_2'(E_2)](E_1-E_2)}. \tag{23}$$

This expression gives the shift of energy level E_1 in the reactant well caused by energy level E_2 in the product well, and vice versa. This equation is the asymmetric counterpart to Eq. 11. As before, a more useful formulation is

$$\Delta E = \frac{h^2\nu_1\nu_2 e^{-2\theta}}{4\pi^2(E_1-E_2)}, \tag{24}$$

which is the counterpart to Eq. 14.

In the asymmetric case, the barrier is represented by the asymmetric Eckart barrier,[32]

$$V(x) = \frac{Ae^{x/b}}{(1+e^{x/b})^2} + \frac{Be^{x/b}}{(1+e^{x/b})}, \tag{25}$$

which reduces to the symmetric barrier (Eq. 16) if B=0 and $A=4V_0$. In Eq. 25 B is the endothermicity of the reaction, i.e., the energy difference between the bottom of the two wells. The barrier height is given by

$$V_0 = \frac{(A+B)^2}{4A}. \tag{26}$$

For the asymmetric barrier, Bell's expression for θ is[32]

$$\theta = \frac{2\pi^2}{h} b\sqrt{2m}\left[A^{1/2}-E^{1/2}-(E-B)^{1/2}\right]. \tag{27}$$

The imaginary frequency for this barrier is

$$\nu_i = \frac{i}{4\pi b}\frac{(A+B)(A-B)}{A\sqrt{2mA}}, \tag{28}$$

Substituting into Eq. 27 results in the more useful expression

$$\theta = \frac{\pi}{h(\nu_i/i)}\frac{(A+B)(A-B)}{2A}\left[1-\left(\frac{E}{A}\right)^{1/2}-\left(\frac{E-B}{A}\right)^{1/2}\right]. \tag{29}$$

Equations 11, 24, and 29 are the formulas necessary for calculation of tunneling rates in asymmetric systems. For real systems, the same considerations as for the symmetric case are also applicable. One further consideration is that the zero-point energy correction (Eq. 22) should also be made for B; i.e.,

$$B_{eff} = B + \tfrac{1}{2}\sum_k (h\nu_{2k}-h\nu_{1k}), \tag{30}$$

where ν_{2k} and ν_{1k} are the frequencies (excluding the reaction coordinate) in the product and reactant wells, respectively. B_{eff} replaces B in Eq. 29.

This computational approach has been implemented in two computer programs (Appendix C). We have used it to calculate several tunneling rates in **3**. The results are shown in Table VIII. These results certainly support our expectation that tunneling is a major factor in the interconversion among cyclobutanediyl minima.

It is also interesting to consider the possibility that tunneling is a factor in the decay of triplet **3** to **4**. Unfortunately, a direct calculation of this tunneling rate is not possible, since there is no well-defined barrier for the process. Figure 8 shows the energy diagram for singlet and triplet **3** along a portion of the singlet inversion pathway. There are an infinity of crossing points between the singlet and triplet adiabatic surfaces, but we take the crossing point shown in Figure 8 to be reasonably representative of these. This

Table VIII. Calculated tunneling rates in **3**.[a]

Reactant	TS	Product	V_0[b] (kcal/mol)	V_{eff} (kcal/mol)	B[b] (kcal/mol)	B_{eff} (kcal/mol)	ν or ν_1[c,d] (cm^{-1})	ν_2[d] (cm^{-1})	ν_i[d] (cm^{-1})	k (s^{-1})
3b	**3a**	**3b**	1.20	0.76			427.8		337.9i	3.2×10^{12}
3c	**3a**	**3c**	0.98	0.56			388.6		292.4i	5.0×10^{12}
3b	**3d**	**3c**	0.58	0.59	0.21	0.18	384.3	351.2	287.0i	1.5×10^{12}
3f	**3e**	**3f**	1.49	0.92			416.6		244.5i	7.9×10^{12}

[a]See text for explanation of notation. [b]Energies from 6-31G* level calculations. [c]ν for symmetric cases, ν_1 for asymmetric case. [d]All frequencies are calculated at the 3-21G level and reduced by 10% for the tunneling rate calculations. Frequencies *before* scaling are shown.

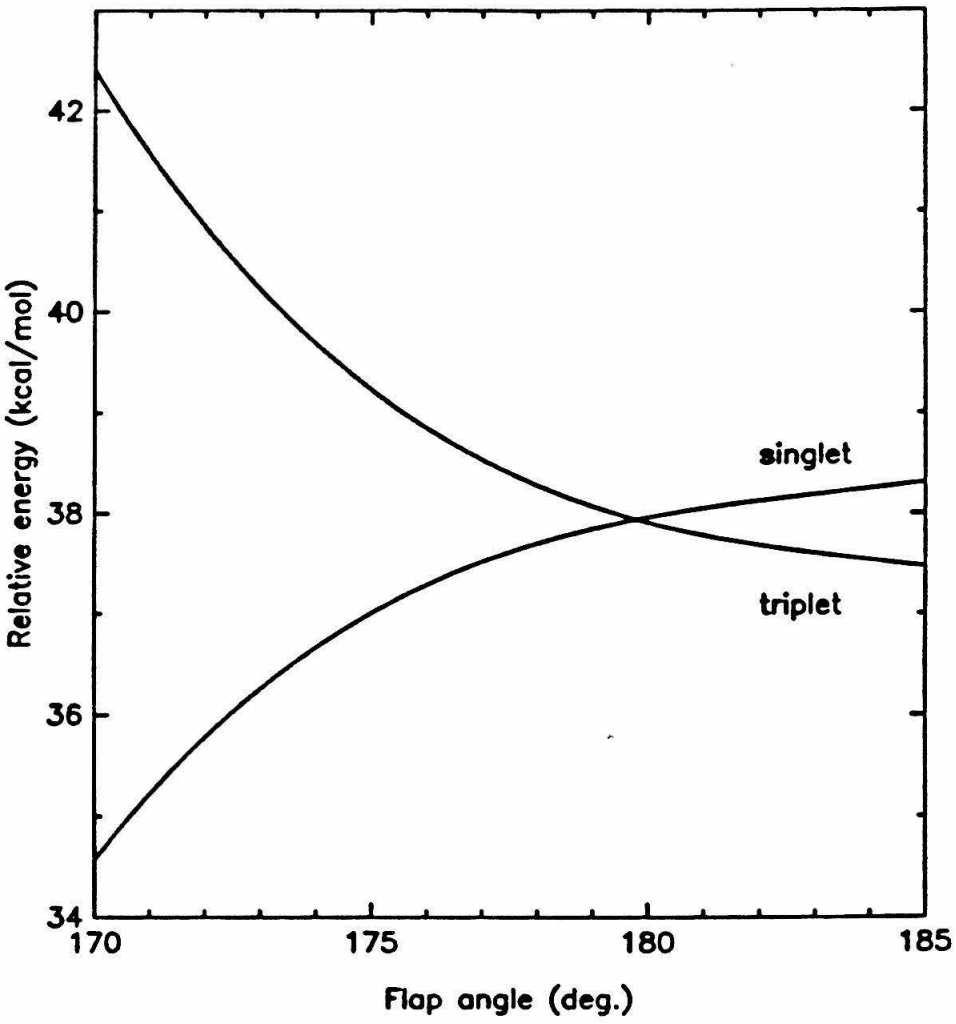


Figure 8. The crossing point between the singlet and triplet potential surfaces along the singlet inversion pathway. Energies are at the 6-31G* level relative to bicyclobutane.

crossing point occurs at an energy of 0.75 kcal/mol above the **3c** minimum (0.9 above **3b**). We note that once this barrier is crossed, there is no additional barrier to form **4**. Compared to the barriers in the tunneling calculations above, the singlet–triplet crossing barrier is similar in height. Also, the process of crossing this barrier involves similar internal motions of the molecule. Thus, we may conclude that a similar tunneling rate may be expected, if not for the fact that the reaction is spin-forbidden. The simplest way to account for this effect is to scale the barrier permeability by an appropriate factor. Data from a variety of sources indicate that simple, unimolecular processes in triplet biradicals have Arrhenius preexponential (A) terms that are smaller by factors of 10^4–10^5 compared to expectations for analogous spin-allowed reactions.[4,29,33] If we scale the tunneling rate by a factor of 10^{-5} to account for this spin forbiddance, we would still obtain a rate on the order of 10^7 s^{-1}. This is certainly fast enough to account for the failure to observe **3** experimentally—it simply decays too fast to allow detection. Of course, these calculations also suggest that if one could prepare singlet **3**, it would tunnel out of its shallow well quite rapidly.

Note that the motions involved in the tunneling process are mainly in H_1 and H_3. Therefore, putting more massive substituents on these positions would slow down the tunneling rate, thus explaining why it was possible to observe the simply substituted systems such as **2-Me** and **2-Et**. For these structures, though, we still see a manifestation of (very much slower) tunneling, in that their decay rates are essentially independent of temperature. Unfortunately we do not have reliable values for the parameters necessary for a tunneling calculation on these substituted systems, especially considering that the tunneling rate calculation is quite sensitive to minor variations in the barrier height and frequencies. We do note, however, that it is possible to obtain for **2-Me** a tunneling rate for the closure reaction comparable to the experimental results (ca. $10^{-2}s^{-1}$), using reasonable estimates for the barrier height (1 kcal/mol—the energy

difference between the C_{2h}-like and the C_s-like structure of 2-Me) and frequencies (148 cm^{-1} for ν, 111i cm^{-1} for ν_i).[34] Thus, this theoretical analysis is not inconsistent with tunneling in the bond-forming reaction of **2-Me**.

Conclusions

The potential energy surfaces of singlet and triplet cyclobutanediyl have been investigated using RHF and TCSCF methods. No significant change was found when the calculations were performed with the 3-21G or 6-31G* basis sets.

At this level of theory, triplet cyclobutanediyl was found to be not planar. Instead, the lowest energy structure has C_{2h} symmetry, and a secondary minimum having C_{2v} symmetry was also found. The two interconvert over a small barrier through a C_s transition state, and it seems quite likely that tunneling is involved in this process.

Singlet cyclobutanediyl was found to be a true minimum, having a C_{2h} structure. A quite unusual reaction pathway for the inversion process of bicyclobutane is proposed. The mechanism does not involve a planar D_{2h} transition state; instead, it passes through the C_{2h} intermediate. The barrier to inversion is calculated to be 39.45 kcal/mol.

The singlet–triplet gap of cyclobutanediyl was calculated to be 1.46 kcal/mol. A crossing point between the triplet and singlet surface was located at an energy 0.75 kcal/mol above the triplet C_{2v} minimum. Crossing this barrier may involve quantum mechanical tunneling, thus providing an explanation for the inability to observe the parent system, triplet **3**. Quite simply, the substituted structures **2-Me** and **2-Et** are stabilized by their *mass*, which greatly slows down the tunneling process and allows their detection by EPR.

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Appendix A: Z-matrices

Complete geometry specifications of the structures described in this chapter are given on the following pages in the form of Z-matrices (Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986). Each row of the matrix corresponds to an atom in the structure. For the row

$$n_1 \quad A \quad n_2 \quad d \quad n_3 \quad \alpha \quad n_3 \quad \delta,$$

the interpretation is as follows:

n_1 the index number of this atom.

A is the atomic symbol for this atom (i.e., C=carbon, H=hydrogen, etc.; X represents a dummy atom used to simplify the coordinate definitions).

n_2 is the index number of a previously defined atom.

d is the distance (in angstroms) between atoms n_1 and n_2.

n_3 is the index number of another previously defined atom.

α is the bond angle (in degrees) defined by atoms n_1, n_2, and n_3, with n_2 as the central atom.

n_4 is the index number of yet another previously defined atom.

δ is the dihedral angle (in degrees) defined by atoms n_1, n_2, n_3, and n_4, with n_2 and n_3 as the central atoms.

3a:

1	C						
2	X	1	1.050856				
3	C	2	1.119461	1	90.000		
4	C	2	1.050856	3	90.000	1	180.000
5	C	2	1.119461	1	90.000	3	180.000
6	H	2	2.118082	3	90.000	1	0.000
7	H	2	2.118082	3	90.000	1	180.000
8	H	3	1.085590	2	125.476	1	90.000
9	H	3	1.085590	2	125.476	1	-90.000
10	H	5	1.085590	2	125.476	1	-90.000
11	H	5	1.085590	2	125.476	1	90.000

3b:

1	X						
2	X	1	1.000000				
3	C	2	1.059387	1	90.000		
4	C	2	1.059387	1	90.000	3	180.000
5	C	2	1.118532	1	90.000	3	90.000
6	C	2	1.118532	1	90.000	3	-90.000
7	H	3	1.070580	2	157.563	1	0.000
8	H	4	1.070580	2	157.563	1	180.000
9	H	5	1.084664	2	125.418	3	90.331
10	H	5	1.084664	2	125.418	4	90.331
11	H	6	1.084664	5	125.418	9	0.000
12	H	6	1.084664	5	125.418	10	0.000

3c:

1	X						
2	X	1	1.000000				
3	C	2	1.059545	1	90.000		
4	C	2	1.059545	1	90.000	3	180.000
5	C	2	1.117996	1	87.110	3	90.000
6	C	2	1.117996	1	87.110	3	-90.000
7	H	3	1.070389	2	160.821	1	0.000
8	H	4	1.070389	2	160.821	1	0.000
9	H	5	1.083716	2	126.170	1	180.000
10	H	5	1.085662	2	124.599	1	0.000
11	H	6	1.083716	2	126.170	1	180.000
12	H	6	1.085662	2	124.599	1	0.000

3d:

1	X						
2	X	1	1.000000				
3	C	2	1.061073	1	90.000		
4	C	2	1.050162	1	90.000	3	180.000
5	C	2	1.118754	1	88.316	3	90.000
6	C	2	1.118754	1	88.316	3	-90.000
7	H	3	1.070640	2	158.241	1	0.000
8	H	2	2.117530	1	89.583	4	0.000
9	H	5	1.085684	6	123.379	3	91.712
10	H	5	1.084613	6	127.506	4	88.416
11	H	6	1.085684	5	123.379	9	0.000
12	H	6	1.084613	5	127.506	10	0.000

3e:

1	C						
2	X	1	1.051522				
3	C	2	1.125583	1	90.000		
4	C	2	1.051522	3	90.000	1	180.000
5	C	2	1.125583	1	90.000	3	180.000
6	H	2	2.118903	3	90.000	1	0.000
7	H	2	2.118903	3	90.000	1	180.000
8	H	3	1.084214	2	125.272	1	90.000
9	H	3	1.084214	2	125.272	1	-90.000
10	H	5	1.084214	2	125.272	1	-90.000
11	H	5	1.084214	2	125.272	1	90.000

3f:

1	X						
2	X	1	1.000000				
3	C	2	1.075470	1	90.000		
4	C	2	1.075470	1	90.000	3	180.000
5	C	2	1.110983	1	90.000	3	90.000
6	C	2	1.110983	1	90.000	3	-90.000
7	H	3	1.073294	2	147.045	1	0.000
8	H	4	1.073294	2	147.045	1	180.000
9	H	5	1.083063	2	125.158	3	89.696
10	H	5	1.083063	2	125.158	4	89.696
11	H	6	1.083063	5	125.158	9	0.000
12	H	6	1.083063	5	125.158	10	0.000

3g:

1	X						
2	X	1	1.000000				
3	C	2	1.064809	1	90.000		
4	C	2	1.052947	1	90.000	3	180.000
5	C	2	1.121772	1	89.137	3	90.000
6	C	2	1.121772	1	89.137	3	-90.000
7	H	3	1.070760	2	156.643	1	0.000
8	H	2	2.119027	1	92.183	4	0.000
9	H	5	1.084228	6	124.217	3	91.198
10	H	5	1.083553	6	126.304	4	89.639
11	H	6	1.084228	5	124.217	9	0.000
12	H	6	1.083553	5	126.304	10	0.000

4:

1	X						
2	X	1	1.000000				
3	C	2	0.764823	1	90.000		
4	C	2	0.764823	1	90.000	3	180.000
5	C	2	1.305948	1	59.992	3	90.000
6	C	2	1.305948	1	59.992	3	-90.000
7	H	3	1.061607	2	133.555	1	180.000
8	H	4	1.061607	2	133.555	1	180.000
9	H	5	1.074534	2	121.484	1	180.000
10	H	5	1.076007	2	123.706	1	0.000
11	H	6	1.074534	2	121.484	1	180.000
12	H	6	1.076007	2	123.706	1	0.000

Table III, $C_3C_1H_1$ angle = 140°:

1	X						
2	X	1	1.000000				
3	C	2	0.761151	1	90.000		
4	C	2	0.760011	1	90.000	3	180.000
5	C	2	1.309874	1	120.553	3	90.000
6	C	2	1.309874	1	120.553	3	-90.000
7	H	3	1.061800	2	134.728	1	0.000
8	H	4	1.061031	2	140.000	1	0.000
9	H	5	1.074627	6	151.938	3	49.073
10	H	5	1.076117	6	93.159	4	131.607
11	H	6	1.074627	5	151.938	9	0.000
12	H	6	1.076117	5	93.159	10	0.000

Table III, $C_3C_1H_1$ angle = 150°:

1	X						
2	X	1	1.000000				
3	C	2	0.753137	1	90.000		
4	C	2	0.765179	1	90.000	3	180.000
5	C	2	1.312899	1	121.116	3	90.000
6	C	2	1.312899	1	121.116	3	-90.000
7	H	3	1.062439	2	135.800	1	0.000
8	H	4	1.061138	2	150.000	1	0.000
9	H	5	1.074789	6	152.467	3	48.643
10	H	5	1.076444	6	92.565	4	132.565
11	H	6	1.074789	5	152.467	9	0.000
12	H	6	1.076444	5	92.565	10	0.000

Table III, $C_3C_1H_1$ angle = 160°:

1	X						
2	X	1	1.000000				
3	C	2	0.745069	1	90.000		
4	C	2	0.778213	1	90.000	3	180.000
5	C	2	1.313827	1	121.462	3	90.000
6	C	2	1.313827	1	121.462	3	-90.000
7	H	3	1.063243	2	136.309	1	0.000
8	H	4	1.062093	2	160.000	1	0.000
9	H	5	1.074902	6	152.846	3	48.291
10	H	5	1.076837	6	92.150	4	132.994
11	H	6	1.074902	5	152.846	9	0.000
12	H	6	1.076837	5	92.150	10	0.000

Table IV, flap angle = 130°

1	X						
2	X	1	1.000000				
3	C	2	0.809344	1	90.000		
4	C	2	0.809344	1	90.000	3	180.000
5	C	2	1.273378	1	65.000	3	90.000
6	C	2	1.273378	1	65.000	3	-90.000
7	H	3	1.065143	2	123.423	1	180.000
8	H	4	1.065143	2	123.423	1	180.000
9	H	5	1.074461	2	121.895	1	180.000
10	H	5	1.076320	2	124.018	1	0.000
11	H	6	1.074461	2	121.895	1	180.000
12	H	6	1.076320	2	124.018	1	0.000

Table IV, flap angle = 140°

1	X						
2	X	1	1.000000				
3	C	2	0.897393	1	90.000		
4	C	2	0.897393	1	90.000	3	180.000
5	C	2	1.230776	1	70.000	3	90.000
6	C	2	1.230776	1	70.000	3	-90.000
7	H	3	1.073970	2	110.318	1	180.000
8	H	4	1.073970	2	110.318	1	180.000
9	H	5	1.075132	2	124.444	1	180.000
10	H	5	1.076302	2	122.432	1	0.000
11	H	6	1.075132	2	124.444	1	180.000
12	H	6	1.076302	2	122.432	1	0.000

Table IV, flap angle = 150°

1	X						
2	X	1	1.000000				
3	C	2	0.936298	1	90.000		
4	C	2	0.936298	1	90.000	3	180.000
5	C	2	1.212305	1	75.000	3	90.000
6	C	2	1.212305	1	75.000	3	-90.000
7	H	3	1.078675	2	110.830	1	180.000
8	H	4	1.078675	2	110.830	1	180.000
9	H	5	1.076056	2	124.737	1	180.000
10	H	5	1.076714	2	122.883	1	0.000
11	H	6	1.076056	2	124.737	1	180.000
12	H	6	1.076714	2	122.883	1	0.000

Table IV, flap angle = 160°

1	X						
2	X	1	1.000000				
3	C	2	0.980703	1	90.000		
4	C	2	0.980703	1	90.000	3	180.000
5	C	2	1.189936	1	80.000	3	90.000
6	C	2	1.189936	1	80.000	3	-90.000
7	H	3	1.081476	2	115.904	1	180.000
8	H	4	1.081476	2	115.904	1	180.000
9	H	5	1.077567	2	125.336	1	180.000
10	H	5	1.077644	2	123.192	1	0.000
11	H	6	1.077567	2	125.336	1	180.000
12	H	6	1.077644	2	123.192	1	0.000

Table IV, flap angle = 170°

1	X						
2	X	1	1.000000				
3	C	2	1.042240	1	90.000		
4	C	2	1.042240	1	90.000	3	180.000
5	C	2	1.148902	1	85.000	3	90.000
6	C	2	1.148902	1	85.000	3	-90.000
7	H	3	1.078166	2	130.923	1	180.000
8	H	4	1.078166	2	130.923	1	180.000
9	H	5	1.081407	2	126.079	1	180.000
10	H	5	1.080302	2	123.906	1	0.000
11	H	6	1.081407	2	126.079	1	180.000
12	H	6	1.080302	2	123.906	1	0.000

Table IV, flap angle = 175°

1	X						
2	X	1	1.000000				
3	C	2	1.057164	1	90.000		
4	C	2	1.057164	1	90.000	3	180.000
5	C	2	1.134194	1	87.500	3	90.000
6	C	2	1.134194	1	87.500	3	-90.000
7	H	3	1.075048	2	141.068	1	180.000
8	H	4	1.075048	2	141.068	1	180.000
9	H	5	1.082817	2	125.777	1	180.000
10	H	5	1.081423	2	124.568	1	0.000
11	H	6	1.082817	2	125.777	1	180.000
12	H	6	1.081423	2	124.568	1	0.000

Table IV, flap angle = 180°

1	X						
2	X	1	1.000000				
3	C	2	1.061756	1	90.000		
4	C	2	1.061756	1	90.000	3	180.000
5	C	2	1.126500	1	90.000	3	90.000
6	C	2	1.126500	1	90.00	3	-90.000
7	H	3	1.072769	2	149.950	1	180.000
8	H	4	1.072769	2	149.950	1	180.000
9	H	5	1.083847	2	125.362	1	180.000
10	H	5	1.082313	2	125.136	1	0.000
11	H	6	1.083847	2	125.362	1	180.000
12	H	6	1.082313	2	125.136	1	0.000

Table IV, flap angle = 185°

1	X						
2	X	1	1.000000				
3	C	2	1.062320	1	90.000		
4	C	2	1.062320	1	90.000	3	180.000
5	C	2	1.123637	1	92.500	3	90.000
6	C	2	1.123637	1	92.500	3	-90.000
7	H	3	1.071653	2	156.192	1	180.000
8	H	4	1.071653	2	156.192	1	180.000
9	H	5	1.084512	2	124.639	1	180.000
10	H	5	1.082490	2	125.851	1	0.000
11	H	6	1.084512	2	124.639	1	180.000
12	H	6	1.082490	2	125.851	1	0.000

Table IV, flap angle = 190°

1	X						
2	X	1	1.000000				
3	C	2	1.061897	1	90.000		
4	C	2	1.061897	1	90.000	3	180.000
5	C	2	1.123174	1	85.000	3	90.000
6	C	2	1.123174	1	85.000	3	-90.000
7	H	3	1.071565	2	159.946	1	0.000
8	H	4	1.071565	2	159.946	1	0.000
9	H	5	1.082310	2	126.572	1	180.000
10	H	5	1.084852	2	123.871	1	0.000
11	H	6	1.082310	2	126.572	1	180.000
12	H	6	1.084852	2	123.871	1	0.000

Table IV, flap angle = 200°

1	X						
2	X	1	1.000000				
3	C	2	1.058655	1	90.000		
4	C	2	1.058655	1	90.000	3	180.000
5	C	2	1.127221	1	80.000	3	90.000
6	C	2	1.127221	1	80.000	3	-90.000
7	H	3	1.071960	2	164.795	1	0.000
8	H	4	1.071960	2	164.795	1	0.000
9	H	5	1.081738	2	127.954	1	180.000
10	H	5	1.085413	2	122.293	1	0.000
11	H	6	1.081738	2	127.954	1	180.000
12	H	6	1.085413	2	122.293	1	0.000

Table IV, flap angle = 210°

1	X						
2	X	1	1.000000				
3	C	2	1.048116	1	90.000		
4	C	2	1.048116	1	90.000	3	180.000
5	C	2	1.139286	1	75.000	3	90.000
6	C	2	1.139286	1	75.000	3	-90.000
7	H	3	1.072279	2	170.378	1	0.000
8	H	4	1.072279	2	170.378	1	0.000
9	H	5	1.081239	2	128.736	1	180.000
10	H	5	1.085592	2	121.221	1	0.000
11	H	6	1.081239	2	128.736	1	180.000
12	H	6	1.085592	2	121.221	1	0.000

Table V, $C_3C_1H_1$ angle = 175°:

1	X						
2	X	1	1.000000				
3	C	2	1.063387	1	90.000		
4	C	2	1.051907	1	90.000	3	180.000
5	C	2	1.123397	1	87.704	3	90.000
6	C	2	1.123397	1	87.704	3	-90.000
7	H	3	1.070920	2	158.372	1	0.000
8	H	4	1.067937	2	175.000	1	0.000
9	H	5	1.084554	6	122.497	3	92.430
10	H	5	1.083139	6	128.007	4	87.814
11	H	6	1.084554	5	122.497	9	0.000
12	H	6	1.083139	5	128.007	10	0.000

Table V, $C_3C_1H_1$ angle = 160°:

1	X						
2	X	1	1.000000				
3	C	2	1.062514	1	90.000		
4	C	2	1.058529	1	90.000	3	180.000
5	C	2	1.124062	1	88.190	3	90.000
6	C	2	1.124062	1	88.190	3	-90.000
7	H	3	1.071681	2	15.711	1	0.000
8	H	4	1.070598	2	160.000	1	0.000
9	H	5	1.084427	6	123.065	3	92.430
10	H	5	1.082598	6	127.445	4	87.814
11	H	6	1.084427	5	123.065	9	0.000
12	H	6	1.082598	5	127.445	10	0.000

2-Me, D_{2h}-like structure:

1	C						
2	X	1	1.050856				
3	C	2	1.119461	1	90.000		
4	C	2	1.050856	3	90.000	1	180.000
5	C	2	1.119461	1	90.000	3	180.000
6	C	2	2.554456	3	90.000	1	0.000
7	C	2	2.554456	3	90.000	1	180.000
8	H	3	1.085590	2	125.476	1	90.000
9	H	3	1.085590	2	125.476	1	-90.000
10	H	5	1.085590	2	125.476	1	-90.000
11	H	5	1.085590	2	125.476	1	90.000
12	H	6	1.086900	1	111.408	3	180.000
13	H	6	1.086900	1	111.408	3	60.000
14	H	6	1.086900	1	111.408	3	-60.000
15	H	7	1.086900	4	111.408	3	180.000
16	H	7	1.086900	4	111.408	3	60.000
17	H	7	1.086900	4	111.408	3	-60.000

2-Me, C_{2h}-like structure:

1	X						
2	X	1	1.000000				
3	C	2	1.059387	1	90.000		
4	C	2	1.059387	1	90.000	3	180.000
5	C	2	1.118532	1	90.000	3	90.000
6	C	2	1.118532	1	90.000	3	-90.000
7	C	3	1.503600	2	157.563	1	0.000
8	C	4	1.503600	2	157.563	1	180.000
9	H	5	1.084664	2	125.418	3	90.331
10	H	5	1.084664	2	125.418	4	90.331
11	H	6	1.084664	2	125.418	9	90.331
12	H	6	1.084664	2	125.418	10	90.331
13	H	7	1.086900	3	111.408	5	180.000
14	H	7	1.086900	3	111.408	5	60.000
15	H	7	1.086900	3	111.408	5	-60.000
16	H	8	1.086900	4	111.408	5	180.000
17	H	8	1.086900	4	111.408	5	60.000
18	H	8	1.086900	4	111.408	5	-60.000

2-Me, C_{2v}-like structure:

1	X						
2	X	1	1.000000				
3	C	2	1.059545	1	90.000		
4	C	2	1.059545	1	90.000	5	180.000
5	C	2	1.117996	1	87.110	5	90.000
6	C	2	1.117996	1	87.110	5	-90.000
7	C	3	1.503600	2	160.821	1	0.000
8	C	4	1.503600	2	160.821	1	0.000
9	H	5	1.083716	2	126.170	1	180.000
10	H	5	1.085662	2	124.599	1	0.000
11	H	6	1.083716	2	126.170	1	180.000
12	H	6	1.085662	2	124.599	1	0.000
13	H	7	1.086900	3	111.408	5	180.000
14	H	7	1.086900	3	111.408	5	60.000
15	H	7	1.086900	3	111.408	5	-60.000
16	H	8	1.086900	4	111.408	5	180.000
17	H	8	1.086900	4	111.408	5	60.000
18	H	8	1.086900	4	111.408	5	-60.000

2-Me, C_s-like structure:

1	X						
2	X	1	1.000000				
3	C	2	1.061073	1	90.000		
4	C	2	1.050162	1	90.000	3	180.000
5	C	2	1.118754	1	88.316	3	90.000
6	C	2	1.118754	1	88.316	3	-90.000
7	C	3	1.503600	2	158.241	1	0.000
8	C	3	1.503600	2	179.170	1	0.000
9	H	5	1.085684	6	123.379	3	91.712
10	H	5	1.084613	6	127.506	4	88.416
11	H	6	1.085684	5	123.379	9	0.000
12	H	6	1.084613	5	127.506	10	0.000
13	H	7	1.086900	3	111.408	5	180.000
14	H	7	1.086900	3	111.408	5	60.000
15	H	7	1.086900	3	111.408	5	-60.000
16	H	8	1.086900	4	111.408	5	180.000
17	H	8	1.086900	4	111.408	5	60.000
18	H	8	1.086900	4	111.408	5	-60.000

Appendix B: Normal Mode Frequencies

Listed below are the calculated (3-21G) normal mode frequencies (in cm^{-1}) of the stationary points on both the singlet and triplet surfaces of **3**. These are the frequencies used in the tunneling calculations, after being reduced by 10% (see Ref. 30b). Those marked with asterisks are used to represent reaction coordinates.

3a	**3b**	**3c**	**3d**	**3e**	**3f**	**3g**	**4**
337.9i*	175.3	200.4	287.0i*	350.2i	228.4	357.0i	455.0
292.4i*	384.3*	351.2*	206.4	244.5i*	416.6*	209.7	778.8
225.8	427.8*	388.6*	408.8	218.6	588.4	398.5	779.4
840.5	816.9	804.9	823.2	854.2	732.9	841.4	828.5
900.5	893.7	899.5	898.2	883.5	885.1	868.9	877.9
927.1	918.1	930.8	930.4	887.5	894.0	889.5	1016.1
936.9	929.3	936.6	931.4	933.2	928.4	932.3	1036.1
975.2	981.3	975.9	976.9	965.4	980.6	971.1	1038.5
1009.1	1041.1	1024.5	1022.0	1023.0	1036.6	1031.1	1133.8
1054.4	1042.7	1060.5	1052.0	1054.6	1068.2	1050.2	1147.3
1152.4	1150.2	1143.1	1148.9	1164.2	1128.8	1155.1	1234.8
1186.5	1226.0	1222.3	1209.1	1204.4	1271.1	1224.6	1254.5
1255.9	1273.4	1265.5	1263.6	1252.5	1285.3	1260.9	1303.0
1375.3	1378.4	1376.9	1376.7	1379.6	1369.8	1377.0	1313.2
1382.7	1378.5	1380.9	1381.3	1383.4	1371.6	1378.4	1315.4
1405.8	1403.6	1403.1	1404.7	1409.2	1383.4	1403.4	1388.2
1615.9	1614.6	1611.1	1614.3	1630.6	1596.3	1622.0	1639.4
1630.8	1628.7	1625.3	1628.7	1644.2	1609.7	1635.8	1667.0
3183.9	3195.7	3193.5	3189.1	3200.7	3221.6	3206.3	3275.8
3188.9	3200.4	3197.6	3193.7	3206.5	3226.1	3211.7	3277.4
3217.4	3232.5	3236.0	3226.2	3238.3	3267.7	3247.0	3362.6
3218.1	3233.0	3237.2	3227.1	3239.7	3268.6	3247.7	3364.0
3413.7	3376.1	3377.8	3377.2	3411.7	3347.3	3376.1	3464.0
3417.5	3379.3	3381.6	3412.9	3415.1	3349.7	3411.2	3479.5

Appendix C: Listing of Computer Programs

On the following pages, the source listings of the two programs used to perform the tunneling calculations are given. GOPHER calculates the tunneling rates for symmetric potentials; GOPHER2 does the same for asymmetric potentials. The programs are written in FORTRAN for interactive use on an IBM PC.

```
C Program GOPHER
C
C Written by Julianto Pranata, California Institute of Technology,
C December 1987.
C
C This program attempts to calculate tunneling rates using the method
C of periodic orbits (W.H. Miller, J.Phys.Chem. 1979, 83, 960). The
C formulas in their most useful forms can be found in JACS 1983, 105,
C 2550 and also in JACS 1984, 106, 4040.
C
      DIMENSION GSFREQ(50),TSFREQ(50)
      DIMENSION ELEVEL(5),RATE(5)
      REAL*4 IMFREQ
      CHARACTER*1 RESP
      DATA CONV/0.002859144/
      DATA PI/3.141592654/
      DATA H/9.5370769E-14/
      DATA R/0.001987192/
C
      WRITE(6,1)
 1    FORMAT(' This is GOPHER, a program to calculate tunneling rates.'
     *      /' Do know how to use the program? [Y/N]')
      READ(5,2) RESP
 2    FORMAT(A1)
      IF ((RESP.EQ.'Y').OR.(RESP.EQ.'y')) GOTO 9
 4    WRITE(6,3)
 3    FORMAT(' GOPHER calculates the tunneling rates between two'/
     *       ' symmetric minima separated by a barrier. You will need'/
     *       ' to supply the vibrational frequencies of both the'/
     *       ' ground state (i.e. the bottom of the well) and the'/
     *       ' transition state (i.e. the top of the barrier). These'/
     *       ' should be supplied in a file called GOPHER.FRQ. List'/
     *       ' the ground state frequencies first, then the'/
     *       ' transition state frequencies. Use negative numbers for'/
     *       ' imaginary frequencies.'/
     *       ' You will also be asked to supply the frequencies of'/
     *       ' ground state mode which leads to the reaction (i.e.'/
     *       ' the reaction coordinate), and the corresponding '/
     *       ' imaginary frequency in the transition state. Finally,'/
     *       ' you will be asked to supply the barrier height.'//
     *       ' Did you get all that? ')
      READ(5,2) RESP
      IF ((RESP.EQ.'N').OR.(RESP.EQ.'n')) GOTO 4
      WRITE(6,5)
 5    FORMAT(' Are you ready to start? (Do you have the GOPHER.FRQ '/
     *       ' file and all the other information?)')
      READ(5,2) RESP
      IF ((RESP.EQ.'Y').OR.(RESP.EQ.'y')) GOTO 9
      WRITE(6,6)
 6    FORMAT(' Please make the necessary preparations. Call me when'/
     *       ' you are ready.')
      GOTO 1000
C
 9    WRITE(6,10)
 10   FORMAT (' How many vibrational modes are there? (Max. = 50)')
      READ(5,*) NMODES
      WRITE(6,13)
 13   FORMAT(' You may have used frequencies calculated by an ab'/
```

```
     *       ' initio molecular orbital method. These frequencies'/
     *       ' are usually too high. You have the option of scaling'/
     *       ' the frequencies by 10 percent. Do you want to do this?')
      READ(6,2) RESP
      SCALE=1.0
      IF ((RESP.EQ.'Y').OR.(RESP.EQ.'y')) SCALE=0.9
      WRITE(6,11)
 11   FORMAT (' Frequencies will be read from file GOPHER.FRQ.')
      OPEN(4,FILE='GOPHER.FRQ',STATUS='OLD')
      OPEN(3,FILE='GOPHER.OUT',STATUS='UNKNOWN')
      READ(4,*) (GSFREQ(I),I=1,NMODES)
      READ(4,*) (TSFREQ(I),I=1,NMODES)
      WRITE(6,12)
 12   FORMAT(' Done reading frequencies.'/)
      WRITE(3,901)
 901  FORMAT(' *** Calculation of tunneling rates ***'//
     *' Ground state frequencies (cm-1):')
      WRITE(3,902) (GSFREQ(I),I=1,NMODES)
 902  FORMAT(10F7.1)
      WRITE(3,903)
 903  FORMAT(/' Transition state frequencies (cm-1):')
      WRITE(3,902) (TSFREQ(I),I=1,NMODES)
      IF (SCALE.EQ.1.0) GOTO 17
      WRITE(3,904)
 904  FORMAT(/' Frequencies will be scaled by 10 percent.'/)
C
C CALCULATE ZERO POINT ENERGIES
C
 17   GSZPE=0.0
      DO 20 I=1,NMODES
      GSFREQ(I)=GSFREQ(I)*SCALE
 20   GSZPE=GSZPE+GSFREQ(I)
      GSZPE=GSZPE*CONV*0.5
C
      TSZPE=0.0
      DO 30 I=1,NMODES
      TSFREQ(I)=TSFREQ(I)*SCALE
      IF (TSFREQ(I).LT.0.0) GOTO 30
      TSZPE=TSZPE+TSFREQ(I)
 30   CONTINUE
      TSZPE=TSZPE*CONV*0.5
C
      WRITE(6,29) GSZPE,TSZPE
      WRITE(3,29) GSZPE,TSZPE
 29   FORMAT(/' Zero point energies (kcal/mol):',F9.4,' (for the ',
     *'ground state)'/32X,F9.4,' (for the transition state)'/)
C
      WRITE(6,31)
 31   FORMAT (' What is the frequency of the reaction mode (in cm-1)?')
      READ(5,*) RXFREQ
      WRITE(6,32)
 32   FORMAT (' The imaginary frequency of the barrier (in cm-1)?')
      READ(5,*) IMFREQ
      WRITE(6,34)
 34   FORMAT(' Do you want to scale these frequencies?')
      READ(5,2) RESP
      IF ((RESP.EQ.'N').OR.(RESP.EQ.'n')) SCALE=1.0
      WRITE(6,33)
```

```
 33   FORMAT (' What is the barrier height (in kcal/mol)?')
      READ(5,*) VZERO
      WRITE(3,911) RXFREQ,IMFREQ
 911  FORMAT(' Reaction coordinate frequencies (cm-1):',F7.1,'  (for',
     *' the ground state)'/40X,F7.1,'i (for the transition state)'/)
      RXFREQ=RXFREQ*SCALE
      IMFREQ=IMFREQ*SCALE
C
C CONSTRUCT ECKART BARRIER
C
      RXFREQ=RXFREQ*CONV*0.5
      VEFF=VZERO-GSZPE+TSZPE+RXFREQ
      IMFREQ=IMFREQ*CONV
C
      WRITE(6,39) VEFF
 39   FORMAT(' Effective barrier height (corrected for z.p.e.)',F9.4,
     *' kcal/mol'/)
      WRITE(3,912) VZERO,VEFF
 912  FORMAT(' Barrier height (kcal/mol):',F9.4,' (original barrier)'/
     *27X,F9.4,' (corrected for zero point energies)'/)
C
C CALCULATE VIBRATIONAL ENERGY LEVELS
C
      DO 40 I=1,5
 40   ELEVEL(I)=(I-0.5)*RXFREQ*2
C
C FIND OUT IF THERE ARE LEVELS ABOVE THE BARRIER
C
      IF (ELEVEL(1).LT.VEFF) GOTO 50
      WRITE(6,41)
 41   FORMAT(' Oh, dear! I just found out that your barrier is too'
     */' small to support any vibrational levels! I cannot do the'/
     *' tunneling calculation. Sorry!')
      GOTO 1000
 50   IF (ELEVEL(2).LT.VEFF) GOTO 60
      INDEX=1
      GOTO 110
 60   IF (ELEVEL(3).LT.VEFF) GOTO 70
      INDEX=2
      GOTO 100
 70   IF (ELEVEL(4).LT.VEFF) GOTO 80
      INDEX=3
      GOTO 100
 80   IF (ELEVEL(5).LT.VEFF) GOTO 90
      INDEX=4
      GOTO 100
 90   INDEX=5
      WRITE(6,91)
 91   FORMAT (' There are 5 or more levels below the barrier.'/
     *' I shall ignore any levels above the fifth in my calculations.'/)
      GOTO 150
 100  WRITE (6,101) INDEX
 101  FORMAT(' There are ',I1,' levels below the barrier.'/
     *' I shall consider them all in my calculations.'/)
      GOTO 150
 110  WRITE(6,111)
 111  FORMAT(' There is only one vibrational level below the barrier.'
     */' A temperature calculation would be meaningless.')
```

```
C
 150  WRITE(3,920)
 920  FORMAT(/' Level',2X,'Energy (kcal/mol)',2X,'    Theta    ',
     *2X,'Delta E (kcal/mol)',2X,'  Rate (s-1)')
C
C LOOP OVER ENERGY LEVELS
C
      DO 200 I=1,INDEX
C
C CALCULATE TRANSMISSION INTEGRAL
C
      THETA=2*PI*(VEFF-SQRT(VEFF*ELEVEL(I)))/IMFREQ
C
C CALCULATE ENERGY LEVEL SPLITTING
C
      IF (THETA.LT.85) GOTO 163
      DELTAE=0.0
      GOTO 164
 163  DELTAE=2*RXFREQ*EXP(-THETA)/PI
C
C CALCULATE TUNNELING RATE
C
 164  RATE(I)=2*DELTAE/H
C
C WRITE RESULTS
C
      WRITE(6,151) I,ELEVEL(I)
 151  FORMAT(' Level no.',I2,'. The energy is',F9.4,' kcal/mol.')
      WRITE(6,156) THETA
 156  FORMAT(' The barrier penetration integral (theta) is',F9.4)
      WRITE(6,152) DELTAE
 152  FORMAT(' The energy splitting is',E12.4,' kcal/mol.')
      WRITE(6,153) RATE(I)
 153  FORMAT(' The tunneling rate is',E12.4,' sec-1.')
C
      WRITE(3,154) I,ELEVEL(I),THETA,DELTAE,RATE(I)
 154  FORMAT(I4,7X,F9.4,8X,F9.4,8X,E12.4,5X,E12.4)
 200  CONTINUE
C
C TEMPERATURE DEPENDENCE CALCULATION
C
      WRITE(6,201)
 201  FORMAT(/' Do you want to calculate temperature dependent rates?')
      READ(5,2) RESP
      IF ((RESP.EQ.'N').OR.(RESP.EQ.'n')) GOTO 1001
      WRITE(3,2003)
 2003 FORMAT (//' Temperature dependent tunneling rates:'
     * //' Temperature (K)',5X,'Rate    (s-1)')
 202  WRITE(6,203)
 203  FORMAT(' What is the temperature? (K)')
      READ(5,*) TEMP
C
C THE PARTITION FUNCTION
C
      Q=0.0
      DO 210 I=1,INDEX
      ELF=(ELEVEL(I)-ELEVEL(1))/(R*TEMP)
      IF (ELF.GT.85) GOTO 210
```

```
      Q=Q+EXP(-ELF)
  210 CONTINUE
C
C BOLTZMANN SUM OF RATES
C
      ARATE=0.0
      DO 300 I=1,INDEX
      ELF=(ELEVEL(I)-ELEVEL(1))/(R*TEMP)
      IF (ELF.GT.85) GOTO 300
      ARATE=ARATE+(RATE(I)*EXP(-ELF))
 300  CONTINUE
      ARATE=ARATE/Q
C
      WRITE(6,301) ARATE
 301  FORMAT(' At that temperature, the tunneling rate is ',E12.4,
     * ' s-1')
      WRITE(3,2004) TEMP,ARATE
 2004 FORMAT(4X,F9.4,7X,E12.4)
      WRITE(6,302)
 302  FORMAT(' Do you want to calculate the rate at another ',
     *'temperature?')
      READ(5,2) RESP
      IF ((RESP.EQ.'Y').OR.(RESP.EQ.'y')) GOTO 202
C
C EXIT PROGRAM
C
 1001 WRITE(6,1002)
 1002 FORMAT(/' You can find the results of this calculation in a '/
     *       ' file called GOPHER.OUT.'//
     *       ' Thank you and have a nice day.')
 1000 STOP
      END
```

```
C Program GOPHER2
C
C Written by Julianto Pranata, California Institute of Technology,
C December 1987.
C
C This program attempts to calculate tunneling rates using the method
C of periodic orbits (W.H. Miller, J.Phys.Chem. 1979, 83, 960). It
C complements the original GOPHER since GOPHER2 calculates tunneling
C rates for asymmetric situations, whereas GOPHER handles only
C symmetric cases.
C
      REAL*4 LFFREQ(50),RTFREQ(50),TSFREQ(50)
      DIMENSION ELEVEL(5),RATE(5)
      REAL*4 IMFREQ,LFZPE,RTZPE,LFFRQ,RTFRQ
      CHARACTER*1 RESP
      DATA CONV/0.002859144/
      DATA PI/3.141592654/
      DATA H/9.5370769E-14/
      DATA R/0.001987192/
C
      WRITE(6,1)
 1    FORMAT(' This is GOPHER2, a program to calculate tunneling rates.'
     *      /' Do know how to use the program? [Y/N]')
      READ(5,2) RESP
 2    FORMAT(A1)
      IF ((RESP.EQ.'Y').OR.(RESP.EQ.'y')) GOTO 9
 4    WRITE(6,3)
 3    FORMAT(' GOPHER2 calculates the tunneling rates between two'/
     *       ' asymmetric minima separated by a barrier. You will need'/
     *       ' to supply the vibrational frequencies of both ground'/
     *       ' states (i.e. the bottom of both wells) and the'/
     *       ' transition state (i.e. the top of the barrier). These'/
     *       ' should be supplied in a file called GOPHER2.FRQ. List'/
     *       ' the reactant frequencies first, then the product'/
     *       ' frequencies, then the transition state frequencies.'/
     *       ' Use negative values for imaginary frequencies.'/
     *       ' You will also be asked to supply the frequencies of'/
     *       ' ground state mode which leads to the reaction (i.e.'/
     *       ' the reaction coordinate), and the corresponding '/
     *       ' imaginary frequency in the transition state. Finally,'/
     *       ' you will be asked to supply the barrier height and the'/
     *       ' endothermicity of the reaction. (The reaction is '/
     *       ' assumed to be endothermic.)'//
     *       ' Did you get all that? ')
      READ(5,2) RESP
      IF ((RESP.EQ.'N').OR.(RESP.EQ.'n')) GOTO 4
      WRITE(6,5)
 5    FORMAT(' Are you ready to start? (Do you have the GOPHER.FRQ '/
     *       ' file and all the other information?)')
      READ(5,2) RESP
      IF ((RESP.EQ.'Y').OR.(RESP.EQ.'y')) GOTO 9
      WRITE(6,6)
 6    FORMAT(' Please make the necessary preparations. Call me when'/
```

```
     *       ' you are ready.')
      GOTO 1000
C
 9    WRITE(6,10)
 10   FORMAT (' How many vibrational modes are there? (Max. = 50)')
      READ(5,*) NMODES
      WRITE(6,13)
 13   FORMAT(' You may have used frequencies calculated by an ab'/
     *       ' initio molecular orbital method. These frequencies'/
     *       ' are usually too high. You have the option of scaling'/
     *       ' the frequencies by 10 percent. Do you want to do this?')
      READ(6,2) RESP
      SCALE=1.0
      IF ((RESP.EQ.'Y').OR.(RESP.EQ.'y')) SCALE=0.9
      WRITE(6,11)
 11   FORMAT (' Frequencies will be read from file GOPHER2.FRQ.')
      OPEN(4,FILE='GOPHER2.FRQ',STATUS='OLD')
      OPEN(3,FILE='GOPHER2.OUT',STATUS='UNKNOWN')
      READ(4,*) (LFFREQ(I),I=1,NMODES)
      READ(4,*) (RTFREQ(I),I=1,NMODES)
      READ(4,*) (TSFREQ(I),I=1,NMODES)
      WRITE(6,12)
 12   FORMAT(' Done reading frequencies.'/)
      WRITE(3,901)
 901  FORMAT(' *** Calculation of tunneling rates ***'//
     *' Reactant frequencies (cm-1):')
      WRITE(3,902) (LFFREQ(I),I=1,NMODES)
 902  FORMAT(10F7.1)
      WRITE(3,907)
 907  FORMAT(/' Product frequencies (cm-1):')
      WRITE(3,902) (RTFREQ(I),I=1,NMODES)
      WRITE(3,903)
 903  FORMAT(/' Transition state frequencies (cm-1):')
      WRITE(3,902) (TSFREQ(I),I=1,NMODES)
      IF (SCALE.EQ.1.0) GOTO 17
      WRITE(3,904)
 904  FORMAT(/' Frequencies will be scaled by 10 percent.'/)
C
C CALCULATE ZERO POINT ENERGIES
C
 17   LFZPE=0.0
      DO 20 I=1,NMODES
      LFFREQ(I)=LFFREQ(I)*SCALE
 20   LFZPE=LFZPE+LFFREQ(I)
      LFZPE=LFZPE*CONV*0.5
C
      RTZPE=0.0
      DO 23 I=1,NMODES
      RTFREQ(I)=RTFREQ(I)*SCALE
 23   RTZPE=RTZPE+RTFREQ(I)
      RTZPE=RTZPE*CONV*0.5
C
      TSZPE=0.0
```

```
      DO 30 I=1,NMODES
      TSFREQ(I)=TSFREQ(I)*SCALE
      IF (TSFREQ(I).LT.0.0) GOTO 30
      TSZPE=TSZPE+TSFREQ(I)
 30   CONTINUE
      TSZPE=TSZPE*CONV*0.5
C
      WRITE(6,29) LFZPE,RTZPE,TSZPE
      WRITE(3,29) LFZPE,RTZPE,TSZPE
 29   FORMAT(/' Zero point energies (kcal/mol):',F9.4,' (for the ',
     *'reactant)'/32X,F9.4,' (for the product)'/32X,F9.4,
     *' (for the transition state)'/)
C
      WRITE(6,31)
 31   FORMAT (' What is the frequency of the reaction mode in the '/
     *        '  reactant (in cm-1)?')
      READ(5,*) LFFRQ
      WRITE(6,37)
 37   FORMAT (' In the product (in cm-1)?')
      READ(5,*) RTFRQ
      WRITE(6,32)
 32   FORMAT (' The imaginary frequency of the barrier (in cm-1)?')
      READ(5,*) IMFREQ
      WRITE(6,34)
 34   FORMAT(' Do you want to scale these frequencies?')
      READ(5,2) RESP
      IF ((RESP.EQ.'N').OR.(RESP.EQ.'n')) SCALE=1.0
      WRITE(6,33)
 33   FORMAT (' What is the barrier height (in kcal/mol)?')
      READ(5,*) VZERO
      WRITE(6,38)
 38   FORMAT(' What is the energy difference between the bottom'/
     *       ' of the wells, the reactant well being LOWER in energy'/
     *       ' (in kcal/mol)?')
      READ(5,*) B
      WRITE(3,911) LFFRQ,RTFRQ,IMFREQ
 911  FORMAT(' Reaction coordinate frequencies (cm-1):',F7.1,'  (for',
     *' the reactant)'/40X,F7.1,'  (for the product)'/40X,F7.1,
     *'i (for the transition state)'/)
      LFFRQ=LFFRQ*SCALE
      RTFRQ=RTFRQ*SCALE
      IMFREQ=IMFREQ*SCALE
C
C CONSTRUCT ECKART BARRIER
C
      LFFRQ=LFFRQ*CONV*0.5
      RTFRQ=RTFRQ*CONV*0.5
      VEFF=VZERO-LFZPE+TSZPE+LFFRQ
      BEFF=B-LFZPE+RTZPE+LFFRQ-RTFRQ
      AEFF=(2*VEFF-BEFF)+2*SQRT(VEFF*(VEFF-BEFF))
      IMFREQ=IMFREQ*CONV
C
      WRITE(6,39) VEFF
```

```
 39   FORMAT(' Effective barrier height (corrected for z.p.e.)',F9.4,
     *' kcal/mol'/)
      WRITE(6,61) BEFF
 61   FORMAT(' Effective endothermicity (corrected for z.p.e.)',F9.4,
     *' kcal/mol'/)
      WRITE(3,912) VZERO,VEFF
 912  FORMAT(' Barrier height (kcal/mol):',F9.4,' (original barrier)'/
     *27X,F9.4,' (corrected for zero point energies)'/)
      WRITE(3,961) B,BEFF
 961  FORMAT(' Endothermicity (kcal/mol):',F9.4,' (original)'/
     *27X,F9.4,' (corrected for zero point energies)'/)
C
C CALCULATE VIBRATIONAL ENERGY LEVELS
C
 947  DO 40 I=1,5
 40   ELEVEL(I)=(I-0.5)*LFFRQ*2
C
C FIND OUT IF THERE ARE LEVELS ABOVE THE BARRIER
C
      IF (ELEVEL(1).LT.VEFF) GOTO 50
      WRITE(6,41)
 41   FORMAT(' Oh, dear! I just found out that your barrier is too'
     */' small to support any vibrational levels! I cannot do the'/
     *' tunneling calculation. Sorry!')
      GOTO 1000
 50   IF (ELEVEL(2).LT.VEFF) GOTO 60
      INDEX=1
      GOTO 110
 60   IF (ELEVEL(3).LT.VEFF) GOTO 70
      INDEX=2
      GOTO 100
 70   IF (ELEVEL(4).LT.VEFF) GOTO 80
      INDEX=3
      GOTO 100
 80   IF (ELEVEL(5).LT.VEFF) GOTO 90
      INDEX=4
      GOTO 100
 90   INDEX=5
      WRITE(6,91)
 91   FORMAT (' There are 5 or more levels below the barrier.'/
     *' I shall ignore any levels above the fifth in my calculations.'/)
      GOTO 150
 100  WRITE (6,101) INDEX
 101  FORMAT(' There are ',I1,' levels below the barrier.'/
     *' I shall consider them all in my calculations.'/)
      GOTO 150
 110  WRITE(6,111)
 111  FORMAT(' There is only one vibrational level below the barrier.'
     */' A temperature calculation would be meaningless.')
C
 150  WRITE(3,920)
 920  FORMAT(/' Level',2X,'Energy (kcal/mol)',2X,'    Theta    ',
     *2X,'Delta E (kcal/mol)',2X,'  Rate (s-1)')
```

```
C
C LOOP OVER ENERGY LEVELS
C
      DO 200 I=1,INDEX
C
C FIND OUT IF LEVELS ARE BELOW PRODUCT WELL
C
      IF (ELEVEL(I).GT.BEFF) GOTO 221
      DELTAE=0.0
      GOTO 164
C
C CALCULATE TRANSMISSION INTEGRAL
C
 221  THETA=PI*(AEFF**2-BEFF**2)*(1.0-SQRT(ELEVEL(I)/AEFF)-
     *      SQRT((ELEVEL(I)-BEFF)/AEFF))/(2*IMFREQ*AEFF)
      IF (THETA.LT.44.0) GOTO 222
      DELTAE=0.0
      GOTO 164
C
C CALCULATE NEAREST MATCHING LEVELS IN PRODUCT WELL
C
 222  ANRT=(ELEVEL(I)-BEFF-RTFRQ)/(2*RTFRQ)
      IF (ANRT.LT.0) THEN
      EHI=(0.5)*RTFRQ*2+BEFF
      ELOW=0.0
      ELSE
      NRT=IFIX(ANRT)
      ELOW=(NRT+0.5)*RTFRQ*2+BEFF
      EHI=(NRT+1.5)*RTFRQ*2+BEFF
      ENDIF
C
C CALCULATE ENERGY LEVEL SPLITTING
C
      DELTAE1=LFFRQ*RTFRQ*EXP(-THETA*2.0)/(PI**2*(EHI-ELEVEL(I)))
      IF (ELOW.EQ.0.0) THEN
      DELTAE2=0.0
      ELSE
      DELTAE2=LFFRQ*RTFRQ*EXP(-THETA*2.0)/(PI**2*(ELEVEL(I)-ELOW))
      ENDIF
      DELTAE=DELTAE1+DELTAE2
C
C CALCULATE TUNNELING RATE
C
  164 RATE(I)=2*DELTAE/H
C
C WRITE RESULTS
C
      WRITE(6,151) I,ELEVEL(I)
 151  FORMAT(' Level no.',I2,'. The energy is',F9.4,' kcal/mol.')
      WRITE(6,156) THETA
 156  FORMAT(' The barrier penetration integral (theta) is',F9.4)
      WRITE(6,152) DELTAE
 152  FORMAT(' The energy splitting is',E12.4,' kcal/mol.')
```

```
      WRITE(6,153) RATE(I)
 153  FORMAT(' The tunneling rate is',E12.4,' sec-1.')
C
      WRITE(3,154) I,ELEVEL(I),THETA,DELTAE,RATE(I)
 154  FORMAT(I4,7X,F9.4,8X,F9.4,8X,E12.4,5X,E12.4)
 200  CONTINUE
C
C TEMPERATURE DEPENDENCE CALCULATION
C
      WRITE(6,201)
 201  FORMAT(/' Do you want to calculate temperature dependent rates?')
      READ(5,2) RESP
      IF ((RESP.EQ.'N').OR.(RESP.EQ.'n')) GOTO 1001
      WRITE(3,2003)
 2003 FORMAT (//' Temperature dependent tunneling rates:'
     * //' Temperature (K)',5X,'Rate    (s-1)')
 202  WRITE(6,203)
 203  FORMAT(' What is the temperature? (K)')
      READ(5,*) TEMP
C
C THE PARTITION FUNCTION
C
      Q=0.0
      DO 210 I=1,INDEX
      ELF=(ELEVEL(I)-ELEVEL(1))/(R*TEMP)
      IF (ELF.GT.85) GOTO 210
      Q=Q+EXP(-ELF)
 210  CONTINUE
C
C BOLTZMANN SUM OF RATES
C
      ARATE=0.0
      DO 300 I=1,INDEX
      ELF=(ELEVEL(I)-ELEVEL(1))/(R*TEMP)
      IF (ELF.GT.85) GOTO 300
      ARATE=ARATE+(RATE(I)*EXP(-ELF))
 300  CONTINUE
      ARATE=ARATE/Q
C
      WRITE(6,301) ARATE
 301  FORMAT(' At that temperature, the tunneling rate is ',E12.4,
     * ' s-1')
      WRITE(3,2004) TEMP,ARATE
 2004 FORMAT(4X,F9.4,7X,E12.4)
      WRITE(6,302)
 302  FORMAT(' Do you want to calculate the rate at another ',
     *'temperature?')
      READ(5,2) RESP
      IF ((RESP.EQ.'Y').OR.(RESP.EQ.'y')) GOTO 202
C
C EXIT PROGRAM
C
 1001 WRITE(6,1002)
```

```
1002 FORMAT(/' You can find the results of this calculation in a '/
     *       ' file called GOPHER2.OUT.'//
     *       ' Thank you and have a nice day.')
1000 STOP
     END
```

Chapter 2

Dimethylenepolycyclobutadienes, the Non-Kekulé Isomers of Classical Acenes

In contrast to localized biradicals, an example of which is the subject of Chapter 1, direct observations of delocalized biradicals are more common.[1] Most delocalized biradicals belong to the class of non-Kelulé molecules, which may be defined as structures for which no formal Kekulé structure can be written.[2] For these structures there are not enough bonds to satisfy standard rules of valence; from a molecular orbital perspective, this translates into the presence of nonbonding molecular orbitals (NBMOs).

Like their localized counterpart, delocalized biradicals can potentially have several low-lying electronic states. However, several qualitative models exist for the prediction of the ground spin states of these structures.[3–5] Among these are: (1) classical structure theory, (2) Hund's first rule, and (3) the "starred/unstarred atom" approach. These methods will be briefly described below.

In classical structure theory, one simply writes down the resonance structure with the maximal pairing of electrons into bonds. For non-Kekulé molecules, this leads (by definition) to some electrons not paired into chemical bonds. Each unpaired electron is assumed to contribute a spin of 1/2 to the total spin (S) of the ground state.

Hund's first rule states that for a given electronic configuration, the state with the maximum total spin has the lowest energy. Application of this rule to determine the spin preference in a molecule requires a knowledge of the number of NBMOs in the molecule. This is usually obtained from a Hückel molecular orbital (HMO) calculation. One then assigns one electron to each NBMO. To satisfy Hund's rule, all these electrons must have parallel spins. Thus, in this approach, the total spin of the ground state is given by the relation

$$S = \frac{n_{NBMO}}{2}, \tag{1}$$

where n_{NBMO} is the number of NBMOs.

The "starred/unstarred atom" approach is applicable only to alternant hydrocarbons (AHs), which are systems in which all the (carbon) atoms can be divided

into two sets, termed "starred" and "unstarred", such that no two atoms in the same set are connected. For such systems, this approach predicts the total spin of the ground state to be given by

$$S = \frac{|n^* - n^\circ|}{2}, \qquad (2)$$

where n* and n° are the numbers of starred and unstarred atoms, respectively.

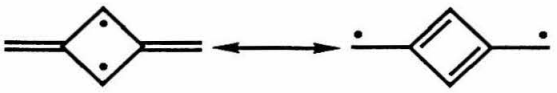
An elegant rationalization of this rule for structures with two NBMOs has been provided by Borden and Davidson.[6] It can be shown that for an AH biradical with unequal numbers of starred and unstarred atoms, the NBMOs can be confined to atoms of the larger set.[7] In most cases this means that the NBMOs are *not* disjoint; i.e., they span common atoms. This results in the presence of high-energy ionic terms in the singlet wave function, corresponding to the simultaneous occupancy of the same atomic orbital (AO) by the two electrons. In the triplet state, the Pauli principle keeps the two unpaired electrons from appearing simultaneously in the same AO. Thus, the triplet state (T) lies below the singlet (S).

When the numbers of starred and unstarred atoms are equal, the NBMOs *are* disjoint, with one NBMO confined to starred, and the other NBMO confined to unstarred atoms. There are no high-energy ionic terms in either the singlet or triplet wave functions. To first order, S and T are degenerate. Typically, higher-order effects preferentially stabilize S, making it the ground state.

In principle, all these models could be applied to systems with more unpaired spins than biradicals. However, experimental tests of these models have been almost entirely confined to biradical structures.[1] One recent exception is the observation of a quintet ground state tetraradical by Berson and co-workers.[8,9]

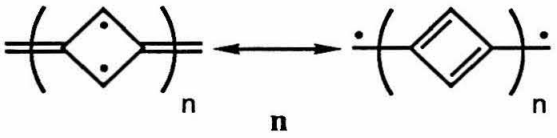
The dimethylenepolycyclobutadienes discussed in this chapter provide a fertile testing ground for these qualitative models. Our interest in these systems arise from the

recent synthesis[10] and spectroscopic characterization[11] of dimethylenecyclobutadiene (**1**), the non-Kekulé isomer of benzene.



1

Building on this system, one can envision a whole series of (4n+2) π systems (**n**). These are the non-Kekulé isomers of the classical acenes (benzene, naphthalene, anthracene, etc.). The term "classical" is used here in the sense that classical, i.e., Kekulé, structures can be written for these molecules; no such structures can be written for **n**. We have called the molecules **n** the "non-Kekulé acenes" to emphasize their isomeric nature to the classical acenes. As discussed below, the qualitative models described above present different predictions about the spin preferences of these systems. This makes **n** a valuable test case for determining the validity and limits of the models.



n

Qualitative Analysis

Classical Structure Theory. All the non-Kekulé acenes can be represented as a chain of cyclobutadienes, with the addition of two singly-bonded methylene groups on the ends (i.e., the resonance structure on the right as shown above). Thus, the resonance structure with maximal pairing of electrons still has two unpaired electrons. Classical structure theory predicts a triplet ground state for all members of this series.

Hund's Rule. The number of NBMOs for **n**, as calculated by HMO, are shown in Table I. It is immediately apparent that there is a parity rule in effect. When n is even, there are n strictly degenerate (E=α) NBMOs; when n is odd, there are (n+1) NBMOs. Using these Hückel NBMOs, Hund's rule leads to the prediction of triplet ground states

Table I. NBMOs of the non-Kekulé acenes (**n**) as obtained from HMO calculations.

Structure	no. of NBMOs
1	2
2	2
3	4
4	4
5	6
6	6

for **1** and **2**, quintets for **3** and **4**, and septets for **5** and **6**. For large n, *very* high spin structures are expected.

Starred/Unstarred Atoms. In Figure 1, we show the starred–unstarred classification of the atoms in **1**–**4**. It is apparent that another manifestation of the parity rule is in effect. When n is odd, there are two more starred atoms than unstarred, and Eq. 2 predicts a triplet ground state. When n is even, there are equal numbers of starred and unstarred atoms, and a singlet ground state is expected.

To summarize, the qualitative models described above produce some fascinating and conflicting predictions for the non-Kekulé acenes. In order to test and expand on these qualitative results, we have performed PPP–SCF–CI calculations[12] on **n**. This method has been used to calculate the singlet–triplet gaps in a variety of conjugated biradicals,[13] and also to calculate the electronic absorption spectra of biradicals with triplet ground states.[14] We emphasize from the start that we do not expect PPP theory to make quantitatively accurate predictions of the properties of **n**. It should, however, predict the basic trends along the series properly and provide a basis for evaluating the highly qualitative theories described above.

Computational Methods. The PPP Approximation

What we currently know as the PPP method was originally presented in the 1950s by Pariser and Parr[12a] and by Pople.[12b] It is one example of the various LCAO–MO methods, where one constructs a set of molecular orbitals (MOs) ϕ_i from linear combinations of atomic orbitals (AOs) χ_μ; i.e.,

$$\phi_i = \sum_\mu c_{i\mu}\chi_\mu \qquad i = 1,2,3,\ldots. \tag{3}$$

The expansion coefficients $c_{i\mu}$ are obtained by a self-consistent-field (SCF) procedure, i.e., as solutions (eigenvectors) of the Roothaan equations,

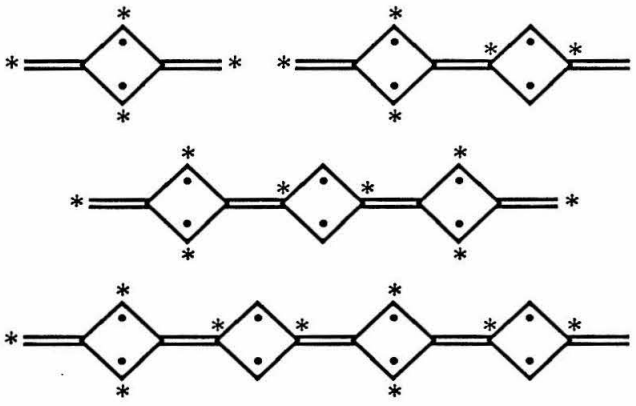


Figure 1. The non-Kekulé acenes as alternant hydrocarbons.

$$\sum_{\nu} F_{\mu\nu} c_{i\mu} = E_i \sum_{\nu} S_{\mu\nu} c_{i\mu} \qquad \mu = 1,2,3,\ldots \quad i = 1,2,3\ldots, \tag{4}$$

where $F_{\mu\nu}$ is a matrix element of the Fock operator (see below), E_i are eigenvalues (corresponding to orbital energies), and $S_{\mu\nu}$ is an overlap matrix element between AOs χ_μ and χ_ν,

$$S_{\mu\nu} = \langle \chi_\mu | \chi_\nu \rangle, \tag{5}$$

$F_{\mu\nu}$ are obtained from the relation

$$F_{\mu\nu} = \langle \chi_\mu | \hat{F} | \chi_\nu \rangle = H^c{}_{\mu\nu} + \sum_{\kappa,\lambda} P_{\kappa\lambda} \left(\langle \chi_\mu \chi_\kappa | e^2 r_{12}^{-1} | \chi_\nu \chi_\lambda \rangle - \tfrac{1}{2} \langle \chi_\mu \chi_\kappa | e^2 r_{12}^{-1} | \chi_\lambda \chi_\nu \rangle \right). \tag{6}$$

The Fock operator thus has terms from the hamiltonian operator of the system,

$$\hat{H} = \sum_i \hat{H}^c{}_i + \sum_{i,j} e^2 r_{ij}^{-1}, \tag{7}$$

with the main difference being that the Fock operator is a one-electron operator, whereas the hamiltonian is a many-electron operator.

In Eq. 6, $H^c{}_{\mu\nu}$ is a matrix element of the core hamiltonian

$$H^c{}_{\mu\nu} = \langle \chi_\mu | \hat{H}^c | \chi_\mu \rangle, \tag{8}$$

which corresponds to the interaction energy between the explicitly-treated electrons and the "core", i.e., the nuclei and any electrons not explicitly treated. The other terms in Eq. 6 correspond to electron–electron repulsions; $P_{\kappa\lambda}$ is an element of the bond-order matrix,

$$P_{\kappa\lambda} = \sum_i b_i c_{i\kappa} c_{i\lambda} \ , \tag{9}$$

where b_i is the occupation number of the MO ϕ_i.

The preceding discussion applies generally to all SCF procedures. What follows are specific for the PPP approximation. The assumptions of this method are:

(1) Only π electrons are treated explicitly. All σ electrons are therefore included in the core.

(2) The AOs χ_μ are assumed to be orthonormal: $S_{\mu\nu}$ is zero except when $\mu=\nu$, in which case it is one. Therefore, the overlap matrix is a unit matrix.

(3) The electron repulsion integrals are identically zero except for coulomb integrals; i.e., when $\mu=\nu$ and $\kappa=\lambda$.

Following these approximations, Eq. 6 becomes

$$F_{\mu\nu} = H^c_{\mu\nu} - \tfrac{1}{2}P_{\mu\nu}\gamma_{\mu\nu} + \delta_{\mu\nu}\sum_{\lambda}P_{\lambda\lambda}\gamma_{\mu\lambda}, \tag{10}$$

where $\delta_{\mu\nu}$ is the Kronecker delta (i.e. $\delta_{\mu\nu}=1$ when $\mu=\nu$ and 0 otherwise), and $\gamma_{\mu\nu}$ is the coulomb integral,

$$\gamma_{\mu\nu} = \langle\chi_\mu\chi_\nu|e^2r_{12}^{-1}|\chi_\mu\chi_\nu\rangle. \tag{11}$$

(4) The diagonal core hamiltonian matrix element is assumed to be

$$H^c_{\mu\mu} = -I_\mu + \sum_{\lambda}Z_\lambda\gamma_{\mu\lambda}, \tag{12}$$

where I_μ is the ionization potential of the atom μ, Z_λ is the "core charge" of the atom λ, which is simply the number of electrons contributed by that atom to the π system.

(5) The off-diagonal core hamiltonian matrix elements are usually assumed to be zero for nonnearest neighbors; i.e.,

$$H^c_{\mu\nu} = \begin{cases} \beta_{\mu\nu} & \text{nearest neighbors} \\ 0 & \text{nonnearest neighbors} \end{cases} \qquad \mu\neq\nu. \tag{13}$$

The final equations for the Fock matrix elements, after all these approximations, are

$$\begin{aligned} F_{\mu\mu} &= -I_\mu + \tfrac{1}{2}P_{\mu\mu}\gamma_{\mu\mu} + \sum_{\lambda\neq\mu}(P_{\lambda\lambda}-Z_\lambda)\gamma_{\mu\lambda} \\ F_{\mu\nu} &= \beta_{\mu\nu} - \tfrac{1}{2}P_{\mu\nu}\gamma_{\mu\nu}\ , \end{aligned} \tag{14}$$

where $\beta_{\mu\nu}$ is zero for nonnearest neighbors.

In a PPP calculation, I_μ, $\beta_{\mu\nu}$, and $\gamma_{\mu\nu}$ are parameterized. I_μ is dependent on the atom type and its hybridization (e.g., an sp^2 oxygen and an sp^3 oxygen would have

different values of I). $\beta_{\mu\nu}$ depends on *pairs* of atoms. $\gamma_{\mu\nu}$ is usually independent of atom types, since it represent electron–electron repulsions, but it does depend on distance.

In the SCF procedure, one starts with an initial guess of the coefficients $c_{i\mu}$. For a PPP calculation, this is usually obtained from a simple Hückel calculation. This initial guess is used to construct the Fock matrix (using Eqs. 9 and 14), which is then used in Eq. 4. Solving Eq. 4 results in improved estimates of the coefficients. The procedure is repeated until no significant changes in $c_{i\mu}$ occur between iterations.

One feature of the PPP method is worth mentioning here. As in Hückel MOs, the MOs obtained by a PPP calculation for alternant hydrocarbons are subject to the pairing theorem.[3,12b,15] This theorem states that the MOs obtained from such calculations come in pairs: for every bonding MO having energy –E, there is an antibonding MO with energy +E. The coefficients of these paired MOs are also related: Coefficients on the starred atoms are the same for the two MOs, whereas coefficients on the unstarred atoms will be equal in magnitude and opposite in sign.

Numerous parameterization schemes have been proposed for the PPP method.[16] In our work we have utilized the parameter set shown in Table II. These are the parameters incorporated into Molnar's "SCFMO" program,[17] on which our programs are based. This parameter set is restricted to conjugated hydrocarbons; there are no parameters for heteroatoms. As a consequence, it is not necessary to specify a value for I_μ. Since all the atoms have identical ionization potentials, nonzero values of I_μ would serve only to shift the orbital energies by the same amount; it does not alter the relative energies of the orbitals. (In this context, I_μ is somewhat analogous to the Hückel α.) Another feature of the parameter set in Table II is the transannular core integral for four-membered rings.[18] This is a nonnearest neighbor interaction term, which serves to upset the pairing theorem described above.

Table II. PPP parameters (eV).

core integrals ($\beta_{\mu\nu}$)	
nearest neighbor	−2.37
transannular (four-membered rings)	−0.40
electron repulsion integrals ($\gamma_{\mu\nu}$)	
one-center coulomb integrals ($\mu=\nu$)	11.35
two-center coulomb integrals ($\mu\neq\nu$)	
$r \leq 1.42$ Å	7.19
1.42 Å $< r \leq$ 2.75 Å	5.77
2.75 Å $< r \leq$ 2.81 Å	4.79
2.81 Å $< r$	14.4/r

Configuration Interaction. The original motivation for the development of the PPP method is to have a simple computational model to calculate electronic spectra of conjugated systems. For such an application, some information about excited states are necessary. This is provided by a configuration interaction (CI) calculation.

As in any CI procedure, a PPP–CI calculation starts out with a set of SCF-optimized MOs, which are obtained by the procedure described above. A number of different "configurations" Φ_m are selected, each corresponding to a particular occupation pattern of the electrons in the MOs. A CI wave function Ψ_i is a linear combination of these configurations; i.e.,

$$\Psi_i = \sum_m C_{im}\Phi_m. \tag{15}$$

The expansion coefficients C_{im} are obtained by solving the equation

$$\sum_n H_{mn}C_{im} = E_i\sum_n S_{mn}C_{im} \qquad m = 1,2,3,\ldots \quad i = 1,2,3,\ldots, \tag{16}$$

where H_{mn} is a matrix element of the hamiltonian operator (Eq. 7; in this case the PPP hamiltonian, with all its approximations as described above) between configurations Φ_m and Φ_n,

$$H_{mn} = \langle\Phi_m|\hat{H}|\Phi_n\rangle, \tag{17}$$

and S_{mn} is the overlap matrix element,

$$S_{mn} = \langle\Phi_m|\Phi_n\rangle. \tag{18}$$

In addition to the expansion coefficients (which are the eigenvectors), the solution of Equation 15 also provides the CI state energies E_i (which are the eigenvalues). Thus, the procedure of obtaining CI wave functions is quite similar to obtaining SCF molecular orbitals, except that no iterations to achieve self-consistency of the coefficients are required.

Electronic spectra are defined by the positions and intensities of various electronic absorptions. The positions of these absorptions are given by the energy difference between an excited CI state Ψ_b and the ground state Ψ_a. The intensities are related to the transition moments, which are computed by calculating the matrix element of the dipole moment operator $\hat{\mathbf{M}}$ between the excited and ground states,

$$\mathbf{M}_{ab} = \langle \Psi_a | \hat{\mathbf{M}} | \Psi_b \rangle, \tag{19}$$

The transition moment $\mathbf{M}_{ab}$ is a vector quantity with components M^x_{ab}, M^y_{ab}, and M^z_{ab}. The intensities are usually reported in terms of oscillator strengths, which are proportional to the square of the transition moment. If the transition frequency ω_{ab} is given in cm^{-1}, the oscillator strength f_{ab} is given by

$$f_{ab} = 1.085\times10^{11}\omega_{ab} \sum_{i=x,y,z} M^i{}_{ab}{}^2. \tag{20}$$

In a typical PPP–CI calculation, one starts with a single reference configuration, corresponding to the ground state. Excited configurations are obtained by single excitations from this reference configuration. In our work, however, a variety of CI calculations are performed. These are (1) excitations within the NBMOs only (which we termed "NCI"); (2) excitations within the NBMOs and single excitations to and from the NBMOs ("NSCI");[14] (3) excitations within NBMOs and single and double excitations to and from the NBMOs ("NSDCI"); (4) excitations within the NBMOs and all single excitations ("SCI"); and (5) excitations within the NBMOs and all single and double excitations ("SDCI"). Within each type of CI (except NCI), we also defined different "levels"; for example, a "2-level SCI" would include all single excitations involving the NBMOs and the two next-highest and two next-lowest molecular orbitals.

Limitations of our programs are (1) only singlet and triplet CI states are calculated; and (2) configurations with more than four unpaired electrons are excluded. This second restriction was imposed to try to keep the dimension of the CI matrix manageable. A

configuration with two unpaired electrons has two states (one singlet and one triplet); with four unpaired electrons there are six (two singlets, three triplets, and one quintet); with six unpaired electrons there are twenty (five singlets, nine triplets, five quintets, and one septet). The number of states increases very rapidly, and we had to restrict the number of unpaired electrons to keep the calculations feasible.[19]

One final point about the CI aspect of the PPP method should be mentioned. The pairing theorem also manifests itself here. Because of the symmetric disposition of the MO energies around a nonbonding level, the excitation energies (which are the diagonal elements of the CI matrix) of the m→n* configuration (obtained by excitation from MO ϕ_m to MO ϕ_{n*}) and the n→m* configuration (where ϕ_m,ϕ_{m*} and ϕ_n,ϕ_{n*} are pairs of MOs as defined by the pairing theorem) are identical. In the CI solution, a state with a contribution from the m→n* configuration will have an equal contribution from the n→m* configuration. In addition, there will be another state with a contribution from the m→n* configuration and an equal contribution, but with opposite sign, from the n→m* configuration. These are called "plus" and "minus" states, respectively.[15b] States of different parity cannot mix, and transitions between states of the same parity are forbidden.[15b] These parity-forbidden transitions are artifacts of the PPP method; they are usually observed as weak transitions in the experimental spectra. In our case, as mentioned above, the use of a nonnearest neighbor core integral serves to upset the pairing theorem. Potentially parity-forbidden transitions are, in fact, predicted by our method to be weakly allowed.

Calculations on the Non-Kekulé Acenes. SCF calculations were performed for **1**–**6**. The molecular orbitals were optimized for a triplet ground state for **1** and **2**, a quintet for **3** and **4**, and a septet for **5** and **6**. The calculations were performed using the optimized geometry of **1** obtained from ab initio calculations, including π-space CI

(square four-membered rings, ring CC bonds 1.471 Å, external CC bonds 1.374 Å).[20a] CI calculations were performed for **1**–**4** as described in the following two sections.

PPP Results for 1

The "monomer" **1** is a crucial structure for this study, since valuable experimental data are available[10,11] for comparison with the computational results. Several ab initio results for **1** also provide useful calibration data.[20] Table III presents the calculated singlet–triplet gaps (a positive number indicates T<S), and Table IV the transition wavelengths and oscillator strengths for **1**. At any level, **1** is calculated to have a substantial triplet preference, as predicted by all the qualitative models and supported by experiment. Several ab initio estimates of the magnitudes of the singlet–triplet gap in **1** have appeared.[20] The values vary somewhat, depending primarily on the geometries used. As mentioned above, we have used the π-CI geometry of Davidson and co-workers. Also, our method calculates the vertical singlet–triplet gap (i.e., singlet and triplet at the same geometry).[20a] The best ab initio estimate of this number is ca. 24 kcal/mol. When the singlet and triplet states are optimized separately (but planarity maintained), a value as low as 8 kcal/mol can be obtained. Our PPP values (Table III) are in good agreement with these estimates. We conclude that PPP has performed quite well in predicting the singlet–triplet gap of **1**.

The prediction of the optical transition in **1** is remarkably good (Table IV). Both the energy and oscillator strength are calculated as accurately as one could possibly hope, given the level of theory involved. The transition is $^3B_{2u} \rightarrow {}^3B_{1g}$, and the dominant configurations involved are shown in Figure 2. The transition in symmetry allowed; its relatively weak oscillator strength arises from the fact that it is a parity forbidden transition (see above). An interesting additional result of these studies is the prediction of no allowed absorption in the UV/vis region for the singlet state of **1**.

Table III. Singlet–triplet gaps[a] (kcal/mol) in non-Kekulé acenes.[b]

	NCI	NSCI	NSDCI	2-level SCI	3-level SCI	4-level SCI
1	19.5	8.2	5.1	20.7		
2	–0.03	–0.02	–0.06	–2.0	–4.0	–1.5
3	8.8	1.8	1.9			
4	–0.02	–0.13				

[a]A positive value indicates T<S. [b]See text for a description of the various levels of theory.

Table IV. Calculated electronic transitions for **1**.[a]

		NSCI	NSDCI	SCI
		Triplet Transitions		
$B_{2u} \rightarrow B_{1g}$	(allowed)[b]	501(0.018)	501(0.018)	504(0.008)
$B_{2u} \rightarrow B_{3u}$	(forbidden)	333	336	363
$B_{2u} \rightarrow B_{2u}$	forbidden)	225	225	302
$B_{2u} \rightarrow B_{3u}$	(forbidden)	306	309	283
$B_{2u} \rightarrow A_g$	(allowed)			277(0.009)
		Singlet Transitions		
$A_g \rightarrow B_{2u}$	(allowed)	1582(0.003)	1351(0.003)	32649(0.0)
$A_g \rightarrow B_{1g}$	(forbidden)	586	551	910
$A_g \rightarrow A_g$	(forbidden)	506	589	514
$A_g \rightarrow B_{1g}$	(forbidden)	243	237	255
$A_g \rightarrow B_{3u}$	(allowed)	204(0.945)	215(0.790)	218(1.331)

[a]In nm; values in parentheses are oscillator strengths. [b]Experimental 506 (0.025) (Ref. 10).

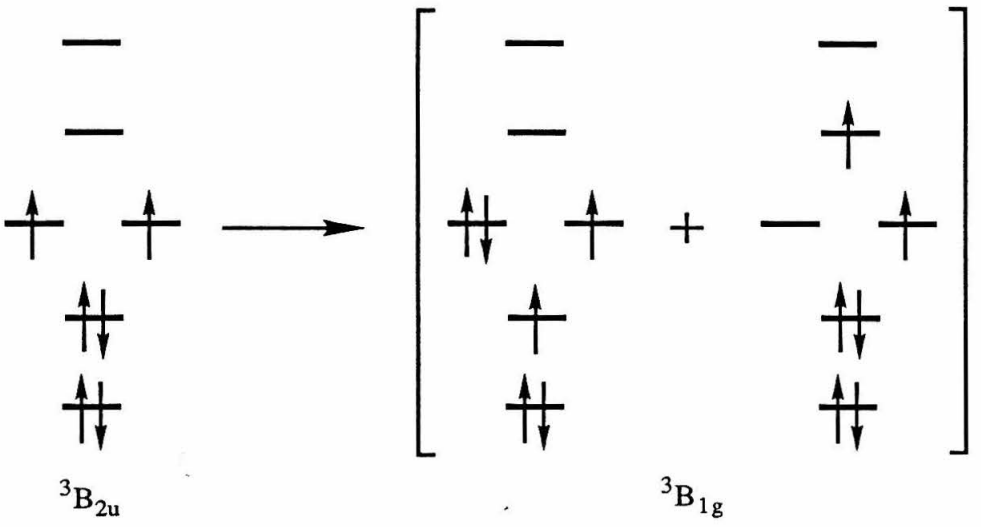


Figure 2. Dominant configurations involved in the first electronic transition of **1**. The molecule is in the *xy*-plane, with the *x*-axis along the long molecular axis.

The important conclusion from the studies on **1** is that PPP theory, as currently applied, is in excellent agreement with all available data on **1**. We thus feel that it should provide meaningful predictions of at least the trends and qualitative features of the non-Kekulé acenes.

PPP Results for 2–6

NBMOs. One of the most fascinating predictions of Hückel theory is the NBMO pattern of **n** (Table I). The prediction is completely confirmed by PPP theory. The orbital energy patterns for **1–6** are shown in Figure 3 and the NBMOs are depicted in Figure 4. These SCF calculations were done for the high-spin states suggested by Table I, i.e., triplet for **1** and **2**, quintet for **3** and **4**, etc. It could be argued that by imposing high-spin states, we forced the NBMO patterns shown. However, SCF calculations on lower-spin states produced unreasonable results, such as orbitals that did not have appropriate symmetries. Calculations on **1** and **2** with quintet spin states produced orbitals that were basically like those in Figure 3.

Examination of the NBMOs (the PPP and Hückel orbitals are essentially identical) reveals another manifestation of the parity rule. When n is even, all n NBMOs are confined exclusively to the CH carbons, and all are antisymmetric with respect to the symmetry plane that is perpendicular to the molecular plane and contains the long axis (Figure 4). These orbitals would appear to suggest the resonance structure on the left of structure **n** (however, see below). When n is odd, there are n orbitals of the type just described (A), plus one more that is symmetric with respect to the previously mentioned symmetry plane (Figure 4).[21]

Singlet–Triplet Gaps. The different qualitative theories make different predictions concerning ground spin states. Both classical structure theory and Hund's rule predict T<S for **2**, while the starred/unstarred atom approach predicts S<T. We have thus made a

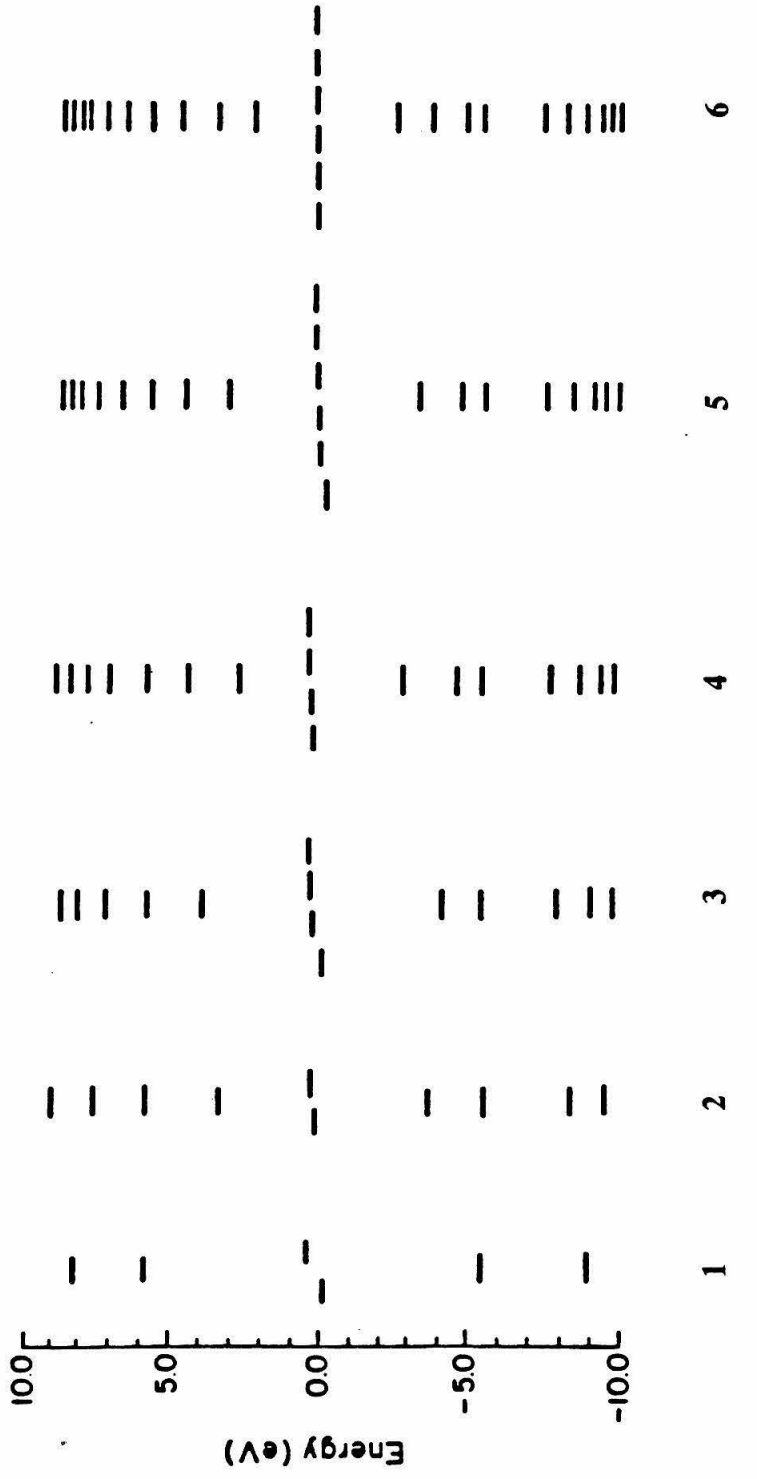


Figure 3. PPP–SCF orbital energies of 1–6.

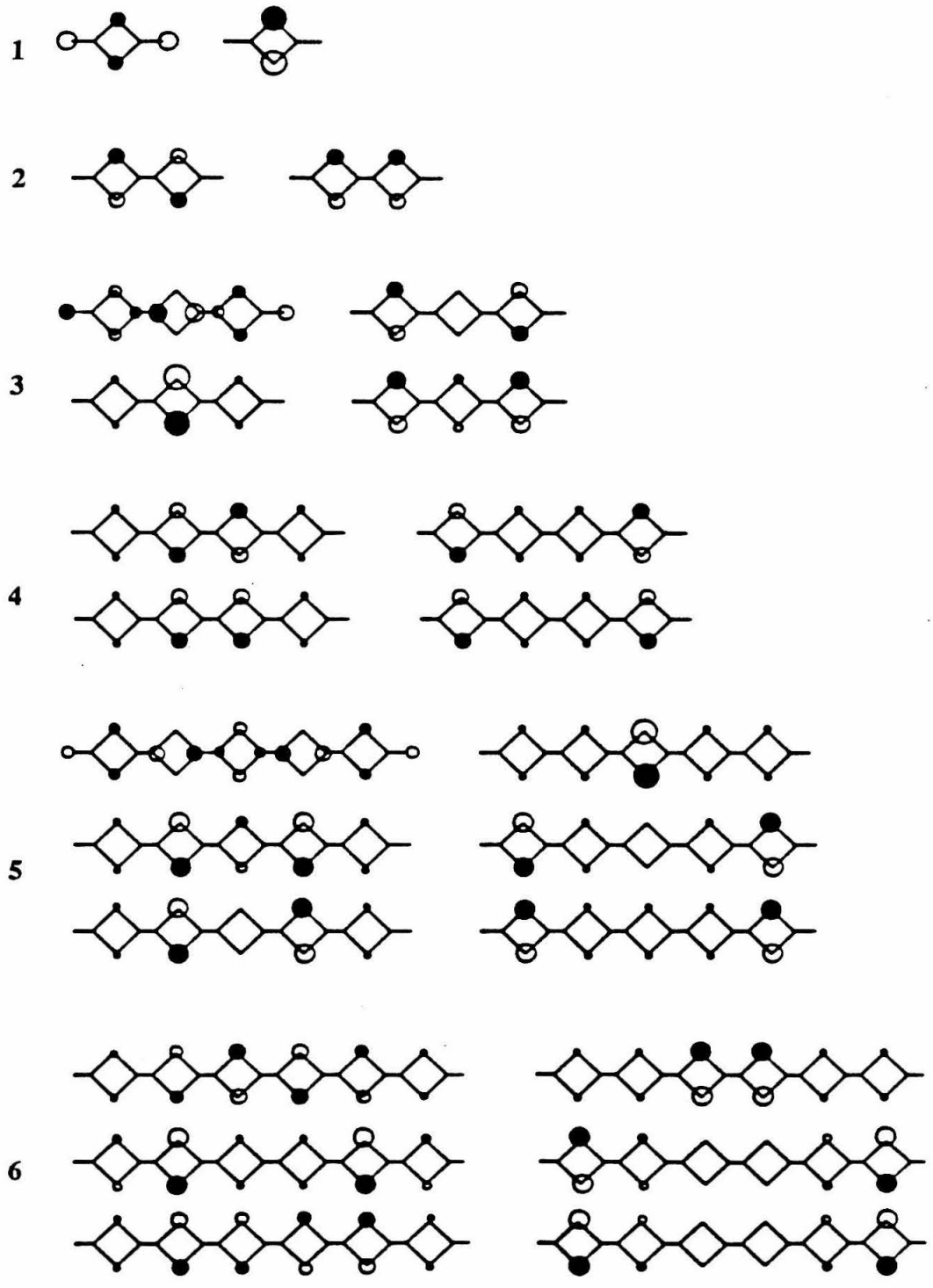


Figure 4. NBMOs of **1**–**6**.

considerable effort to evaluate the spin preference of **2**. *All* levels of PPP–CI theory predict S<T, consistent only with the starred/unstarred atom approach. The results are summarized in Table III. The gap is quite small at lower levels of theory, but increases substantially as more CI is included.

We have also performed CI calculations at several levels on **3** and **4** (Table III). Again a parity rule is evident. When n is even, we obtain S<T; when n is odd, we obtain T<S. Only the starred/unstarred atom approach predicts this trend. Of course, since we have not considered the quintet state in our calculations, we have not disproved the possibity of a quintet ground state (as predicted by Hund's rule) for these molecules. However, since it fails to predict the spin preference in **2** correctly, one would question the applicability of Hund's rule to the higher non-Kekulé acenes.

Electronic Transitions for 2. An important result of these studies is that **2** should have a singlet ground state, and thus may not be detectable by EPR spectroscopy. Given this result, the remarkable accuracy of the PPP–CI prediction of the electronic transition in **1** becomes especially important to experimental efforts to synthesize and detect **2**. One might expect that PPP–CI should also provide a reasonable estimate of the electronic transitions in **2**, and we have calculated both singlet and triplet transitions at several levels of theory. The results are summarized in Table V.

For both singlet and triplet **2**, the first allowed electronic transitions are at substantially longer wavelengths than in analogous spin states of **1**, as expected. Like **1**, the first triplet–triplet transition of **2** is at lower energy than the first singlet–singlet transition. Not surprisingly, for a more complex molecule such as this, there is some scatter among the various methods. Nevertheless, we feel that the prediction of weak (symmetry-allowed, parity-forbidden) transitions at ca. 580–640 nm for triplet **2** and 420–460 nm for singlet **2** will provide valuable guideposts for experimental efforts.

Table V. Calculated electronic transitions for **2**.[a]

		NSCI	NSDCI	2-level SCI	3-level SCI	4-level SCI
				Triplet Transitions		
$B_{3u} \rightarrow B_{3u}$	(forbidden)	[b]	[b]	766	755	758
$B_{3u} \rightarrow A_g$	(allowed)	[b]	[b]	592(0.004)	661(0.001)	623(0.0)
$B_{3u} \rightarrow B_{1g}$	(allowed)	842(0.010)	840(0.010)	635(0.011)	637(0.007)	584(0.006)
$B_{3u} \rightarrow B_{2u}$	(forbidden)	819	816	624	623	572
$B_{3u} \rightarrow A_g$	(allowed)	[b]	[b]	474(0.002)	498(0.001)	492(0.002)
				Singlet Transitions		
$A_g \rightarrow A_g$	(forbidden)	[b]	[b]	409	492	493
$A_g \rightarrow B_{1g}$	(forbidden)	597	596	453	414	444
$A_g \rightarrow B_{2u}$	(allowed)	596(0.011)	594(0.010)	455(0.009)	417(0.005)	443(0.005)
$A_g \rightarrow B_{3u}$	(allowed)	[b]	[b]	[b]	415(0.0)	429(0.003)
$A_g \rightarrow A_g$	(forbidden)		429	367	366	355

[a]In nm; values in parentheses are oscillator strengths. [b]No configurations of excited-state symmetry at this level of theory.

Discussion

Non-Kekulé molecules have been the focus of much research effort in recent years, with one of the major goals being the development of simple methods for predicting the basic properties of such structures. The non-Kekulé acenes provide a fertile testing ground for the various methods. If we consider the PPP results to be semiquantitatively reliable, then a straightforward qualitative approach emerges. HMO theory correctly predicts the number of NBMOs and their nodal properties. In order to determine the preferred spin states, one simply counts the numbers of starred and unstarred atoms. At least for the non-Kekulé acenes, this simple combination of an HMO calculation with a counting of starred and unstarred atoms provides qualitatively correct information.[22]

The underlying reasion that the starred/unstarred atom approach is successful is provided by the Borden–Davidson analysis. In most cases, the starred/unstarred atom approach correctly predicts whether or not the NBMOs are disjoint. Exceptions arise in structures involving unions of odd AHs at inactive sites,[6] an arrangement that is not present in **n**. It can easily be shown that even for non-Kekulé acenes with more than two NBMOs, the disjoint NBMO analysis holds. Referring to Figure 4, it is apparent that when n is even (**4** and **6**), a completely disjoint set of NBMOs can be obtained simply by confining each NBMO to only one ring. There would be one such NBMO for each ring. Since all the NBMOs are disjoint, a singlet ground state is expected. When n is odd (**3** and **5**) the situation is more complex. The n orbitals of A symmetry can be localized in the same manner as the NBMOs in the even n case. For the NBMO of S symmetry, a distinctive nodal pattern emerges. There are nodal planes perpendicular to the molecular plane and to the long axis, which contain the unstarred CH groups. If one numbers the rings from left to right, these nodes bisect the even-numbered rings. Using **5** as an example, there are two such nodal planes in the S NBMO. Clearly, the two A NBMOs

localized to these even-numbered rings are disjoint with regard to the S NBMO, while the other three are not. One thus has a set of four NBMOs (one S and three A) that share common atoms, and two others that are fully disjoint. A perhaps naive extension of the Borden–Davidson analysis places parallel spins in the four nondisjoint NBMOs, and the opposite spins in the two disjoint NBMOs. One would have, for example, four α spins and two β spins, thus producing a triplet state.

The present work has uncovered several interesting features of the non-Kekulé polyacenes, but perhaps the most intriguing is the parity rule. One can rationalize the parity rule using simple structural arguments. For non-Kekulé molecules, there are two structural prototyes. One is trimethylenemethane (TMM). It has three starred and one unstarred atoms, and serves as the prototypical high-spin non-Kekulé molecule. In fact, all high-spin non-Kekulé molecules contain an embedded TMM substructure. The prototypical low-spin non-Kekulé molecule is tetramethyleneethane (TME), with three starred and three unstarred atoms. TME can be thought of as two allyl radicals joined at the allyl NBMO. Both TMM and TME contain two NBMOs, which are disjoint in the case of TME but not in the case of TMM.

TMM **TME**

The non-Kekulé acenes can be built up from these two smaller, non-Kekulé units. It is simpler to consider the even n structures first. The even n molecules can be built up entirely from TMEs, as shown in Figure 5. Since TME is low spin, and since the individual TME units are isolated from one another, the whole molecule is low-spin. The NBMOs of Figure 4 support this view. For even n, the NBMOs appear to be just linear combinations of isolated *p* orbitals on the CH groups. However, they are, in fact, linear combinations of allyl NBMOs, as suggested by the structures in Figure 5. In Figure 4, *p*

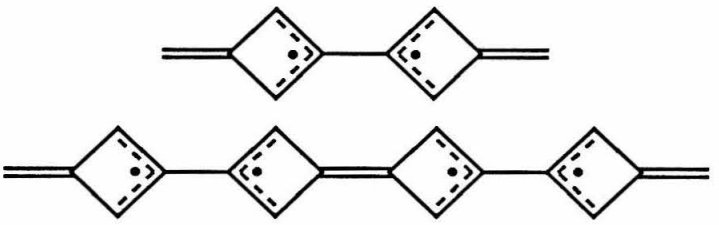


Figure 5. Even n non-Kekulé acenes built up from TME units.

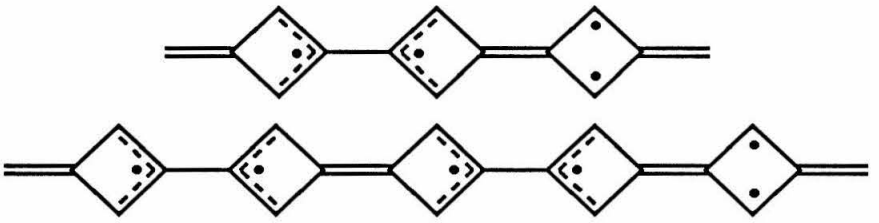


Figure 6. Odd n non-Kekulé acenes built up from TME units and one TMM unit.

orbitals in the same ring (even n) are *always* out of phase with one another, as expected for an allyl NBMO. If these NBMOs were just linear combinations of isolated *p* orbitals, one would have expected some in-phase pairings of orbitals in the same ring.

When n is odd, one can build up (n–1)/2 TMEs, leaving one remaining ring. This ring must take the form of a TMM (Figure 6). Thus, there will always be a high-spin non-Kekulé fragment in these molecules, and a triplet ground state is expected. The NBMOs in Figure 4 support this analysis. There are n NBMOs of the allyl type. The extra NBMO has the form of the left member of the TMM NBMOs shown in Figure 7, in the sense that they are symmetric with respect to a symmetry plane perpendicular to the molecular plane and containing a C_2 axis of the molecule. (The right member is like an allyl NBMO and is antisymmetric with respect to the aforementioned symmetry plane.)

The simple structural analysis summarized in Figures 5 and 6 leads to correct predictions of the number of NBMOs, their nodal properties, and the ground spin states of all the non-Kekulé polyacenes. It also suggests another factor to be considered: nonplanarity. The barrier to rotation about the central C–C bond in TME is probably quite small, and, in fact, the ground state structure may be orthogonal (two allyl units at a 90° angle).[1f,23] This suggests another intriguing structure for the non-Kekulé acenes (Figure 8) with alternating eight-carbon units in orthogonal planes. Conjectures about the ground spin states and optical properties of such a structure would be highly speculative at this stage.

Conclusions

We have described structures designated by **n** as the non-Kekulé analogues of the classical acenes. Even the monomer (**1**) has quite interesting properties, and it is clear that the higher homologues will possess fascinating optical, electronic, and magnetic properties. Perhaps most interestingly, these molecules do not show a simple,

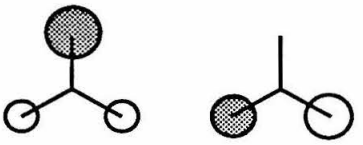


Figure 7. NBMOs of TMM.

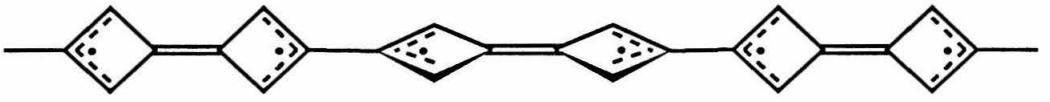


Figure 8. Nonplanar structure for non-Kekulé acenes.

progressive change in properties with increasing n. Rather, a parity rule emerges, in which even n and odd n members of the series are expected to have qualitatively different properties. We have also shown that simple structural arguments can completely rationalize the results obtained from quantitative calculations.

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(21) The structures with odd n and n>1 present an apparent violation of the rule[7] that in alternant hydrocarbons with unequal numbers of starred and unstarred atoms, the NBMOs are confined to the larger set. Recall, however, that this rule was derived for structures with only two NBMOs, while **3** and **5** have four and six NBMOs, respectively.

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Appendix A: PPP Results for Some Test Molecules

In order to obtain some indication of the reliability of our PPP calculations, we performed calculations on trimethylenemethane (TMM), square cyclobutadiene, and *m*-xylylene. These calculations were done at regular geometries with CC bond lengths of 1.40 Å. The results of these calculations are presented below, along with values obtained by other means.

	PPP	ab initio	experiment
Singlet–Triplet Gaps (kcal/mol)			
TMM (T<S)	13.3 (NSCI) 21.9 (SCI) 19.6 (SDCI)	21.2,[a] 26.4[b]	
cyclobutadiene (S<T)	9.2×10^{-5} (NSCI) 8.1 (SCI) 9.0 (SDCI)	7.3,[c] 14.0,[d] 10[e]	
Triplet–Triplet absorptions (nm)			
TMM	302 (NSCI) 323 (SCI) 339 (SDCI)	266[b]	~300–350[f]
m-xylylene	391 (NSCI) 451 (SDCI)		442[g]

[a]Dixon, D. A.; Dunning, T. A.; Eades, R. A.; Kleier, D. A. *J. Am. Chem. Soc.* **1981**, *103*, 2878–2880. [b]Davis, J. H.; Goddard, W. A. III *J. Am. Chem. Soc.* **1977**, *99*, 4242–4247.[c]Kollmar, H.; Staemler, V. *J. Am. Chem. Soc.* **1977**, *99*, 3583–3587. [d]Borden, W. T.; Davidson, E. R.; Hart, P. *J. Am. Chem. Soc.* **1978**, *100*, 388–392. [e]Jafri, J. A.; Newton, M. D. *J. Am. Chem. Soc.* **1978**, *100*, 5012–5017. [f]Value for two derivatives of TMM: Turro, N. J.; Mirbach, M. J.; Harrit, N.; Berson, J. A.; Platz, M. S. *J. Am. Chem. Soc.* **1978**, *100*, 7653–7658. [g]Migirdicyan, E.; Baudet, J. *J. Am. Chem. Soc.* **1975**, *97*, 7400–7407.

Appendix B: Listing of Computer Programs

On the following pages, the source listings of the two programs used to perform the PPP calculations are given. PPPSCF constructs the SCF molecular orbitals, while PPPCI performs the CI calculations based on these orbitals. These programs were originally based on Molnar's "SCFMO" program (Molnar, S.P. QCPE Program No. 314, Indiana University, Bloomington, IN, 1976).

```
C  PROGRAM PPPSCF
C  PROGRAM TO CALCULATE SCF MOLECULAR ORBITALS USING PPP THEORY
C  WRITTEN BY JULIANTO PRANATA, CALIFORNIA INSTITUTE OF TECHNOLOGY,
C  NOVEMBER 1985
C  BASED ON QCPE 314
      DIMENSION H(30,30),F(30,30),FDIAG(30),C(30,30),G(30,30),Z(30)
      DIMENSION X(30),Y(30),TITLE(14)
C  DEFINITIONS: H  =CORE INTEGRALS
C               G  =ELECTRON REPULSION INTEGRALS
C               F  =ENERGY MATRIX
C               C  =EIGENVECTORS ON F (M.O. COEFFICIENTS)
C               Z  =NUCLEAR CHARGE
C               X,Y=NUCLEAR COORDINATES
      KMOLS = 0
C  SUBROUTINES SCFCON AND SCFMA ARE FOR INPUT OF DATA
      CALL SCFCON(NMOLS,EPS,HAFGAM,BETA,TITLE)
 76   KMOLS = KMOLS+1
      IF (KMOLS-NMOLS) 77,77,78
 77   CONTINUE
      CALL SCFMA(N,M,MM,H,F,FDIAG,G,Z,X,Y)
      WRITE (3,35) N,M,MM
 35   FORMAT (3I3)
C SCF ITERATIONS ARE TERMINATED AFTER A SPECIFIED NUMBER OF CYCLES
      READ (1,99) ITER
 99   FORMAT (I4)
      WRITE (2,501) ITER
 501  FORMAT ( 'NO. CYCLES IN SCF ITERATION     =',I6)
C  SCFMOD ALLOWS MODIFICATION OF PARAMETERS FROM DEFAULT VALUES
      CALL SCFMOD(N,H,F,FDIAG,G,Z)
C  SCFPRI WRITES H,G,AND Z IN OUTPUT FILE
      CALL SCFPRI(N,H,G,Z)
      NIT = 0
C  SCFJAC AND FOLLOWING SUBROUTINES DIAGONALIZE THE ENERGY MATRIX
C  ITERATIVELY
 17   CALL SCFJAC(N,F,FDIAG,C,NIT,EPS)
      CALL SCFARR(N,F,FDIAG,C)
      CALL SCFNFM(N,M,MM,F,FDIAG,C,G,Z,HAFGAM)
      CALL SCFTRF(N,F,FDIAG,C)
      NIT=NIT+1
      IF (NIT-ITER) 17,17,18
C  SCFPIE CALCULATES THE PI ELECTRON ENERGY, DIPOLE MOMENT, AND THE
C  DENSITY AND BOND ORDER MATRIX. SCFPRN PRINTS THE ORBITAL ENERGIES
C  AND COEFFICIENTS
 18   CALL SCFPIE(N,M,MM,F,C,G,Z,X,Y)
      CALL SCFPRN(N,FDIAG,C)
      CALL SCFHCR(N,H,G,Z)
 701  FORMAT (6F12.8)
      DO 720 I=1,N
 720  WRITE (3,701) (H(I,J),J=1,N)
      DO 730 I=1,N
 730  WRITE (3,701) (G(I,J),J=1,N)
      DO 740 I=1,N
 740  WRITE (3,701) (C(I,J),J=1,N)
      WRITE (3,701) (X(I),I=1,N)
      WRITE (3,701) (Y(I),I=1,N)
      GO TO 76
 78   STOP
      END
```

```
C
      SUBROUTINE SCFCON(NMOLS,EPS,HAFGAM,BETA,TITLE)
      DIMENSION TITLE(14)
      READ (1,102) (TITLE(I),I=1,14)
 102  FORMAT(14A4)
      WRITE (2,103) (TITLE(I),I=1,14)
      WRITE (3,102) (TITLE(I),I=1,14)
 103  FORMAT(///,5X,14A4)
      EPS=1.0E-16
      HAFGAM=5.675
      BETA=-2.37
      READ(1,100)NMOLS
 100  FORMAT(I3)
      WRITE(2,101) NMOLS
 101  FORMAT(//'NUMBER OF MOLECULES    =',I6)
      RETURN
      END
C
      SUBROUTINE SCFMA(N,M,MM,H,F,FDIAG,G,Z,XCRD,YCRD)
      DIMENSION H(30,30),F(30,30),G(30,30),FDIAG(30),Z(30),X(30),Y(30)
      DIMENSION NATM(30),XCRD(30),YCRD(30)
      READ (1,99) N,M,MM
 99   FORMAT(3I3)
      WRITE(2,200)N,M,MM
 200  FORMAT ( ' NUMBER OF ATOMS IN PI-SYSTEM    =',I6,
     *       / ' NUMBER OF DOUBLY OCCUPIED M.O.S =',I6,
     *       / ' NUMBER OF SINGLY OCCUPIED M.O.S =',I6)
      READ (1,*) (X(I),I=1,N)
      READ (1,*) (Y(I),I=1,N)
      READ (1,*) (NATM(I),I=1,N)
      DO 550 I=1,N
      FDIAG(I)=0.0
      DO 550 J=1,N
      F(I,J)=0.0
 550  H(I,J)=0.0
      DO 10 I=1,N
      ID = NATM(I)
      XD = X(ID)
      YD = Y(ID)
      YCRD(I) = YD
      XCRD(I) = XD
      DO 10 J=I,N
      IF (I-J) 12,13,12
 13   G(I,J)=11.35
      GO TO 10
 12   JD = NATM(J)
      XC = X(JD)
      YC = Y(JD)
      D = SQRT((XC-XD)**2+(YC-YD)**2)
      IF (D-2.81) 14,14,51
 51   G(I,J) = 14.4/D
      G(J,I) = G(I,J)
      GO TO 10
 14   IF (D-2.75) 15,15,52
 52   G(I,J)=4.97
      G(J,I)=G(I,J)
      GO TO 10
 15   IF (D-1.42) 16,16,17
```

```
 17   G(I,J)=5.77
      G(J,I)=G(I,J)
      GO TO 10
 16   G(I,J)=7.19
      G(J,I)=G(I,J)
 10   CONTINUE
      IUPP=N-1
      DO 20 I=1,IUPP
      JLOW=I+1
      DO 20 J=JLOW,N
      IF (G(I,J)-7.0) 20,20,21
 21   F(J,I)=-2.37
      F(I,J)=-2.37
      H(I,J)=-2.37
      H(J,I)=-2.37
 20   CONTINUE
      DO 113 J=1,N
 113  Z(J)=1.0
      WRITE(2,903)
 903  FORMAT (/5X,8H ATOM(I),5X,13H X-COORDINATE,5X,14H Y-COORDINATE )
      DO 1003 I=1,N
      WRITE (2,904) I,XCRD(I),YCRD(I)
  904 FORMAT (8X,I2,10X,F8.3,10X,F8.3)
 1003 CONTINUE
      RETURN
      END
C
      SUBROUTINE SCFMOD(N,H,F,FDIAG,GAM,Z)
      DIMENSION F(30,30),H(30,30),FDIAG(30),GAM(30,30),Z(30)
      WRITE (2,200)
 200  FORMAT (/)
 100  FORMAT(I2)
 101  FORMAT(I1)
 102  FORMAT(2I2,F7.3)
 103  FORMAT(I2,F3.1)
 104  FORMAT (3X,I2,1X,F4.1)
 202  FORMAT (1X,2I2,F7.3)
 7    READ (1,101) LAB
      IF (LAB) 9,8,9
 9    IF (LAB-2) 66,67,68
 66   WRITE(2,130)
 130  FORMAT (16H H MODIFICATIONS)
      GO TO 69
 67   WRITE (2,131)
 131  FORMAT (16H G MODIFICATIONS)
      GO TO 69
 68   WRITE (2,132)
 132  FORMAT (16H Z MODIFICATIONS)
 69   READ (1,100) NITEM
      WRITE (2,501) NITEM
 501  FORMAT( I6,' VALUES MODIFIED')
      DO 20 K=1,NITEM
      GO TO (10,11,12) LAB
 10   READ (1,102) I,J,F(I,J)
      H(I,J)=F(I,J)
      WRITE (2,202) I,J,F(I,J)
      IF (I-J) 120,20,120
 120  CONTINUE
```

```
      F(J,I)=F(I,J)
      H(J,I)=H(I,J)
      GO TO 20
 11   READ (1,102) I,J,GAM(I,J)
      WRITE (2,202) I,J,GAM(I,J)
      IF (I-J) 121,20,121
 121  CONTINUE
      GAM(J,I)=GAM(I,J)
      GO TO 20
 12   READ (1,103) J,Z(J)
      WRITE (2,104) J,Z(J)
 20   CONTINUE
      GO TO 7
 8    DO 13 J=1,N
 13   FDIAG(J)=F(J,J)
      RETURN
      END
C
      SUBROUTINE SCFJAC(N,A,ADIAG,U,NIT,EPS)
      DIMENSION A(30,30),U(30,30),ADIAG(30)
      IF (NIT) 10,999,10
 999  DO 8 J=1,N
      DO 9 I=1,N
 9    U(I,J)=0.0
 8    U(J,J)=1.0
 10   AMAX=0.0
      DO 11 I=2,N
      JUP = I-1
      DO 11 J=1,JUP
      AII=ADIAG(I)
      AJJ=ADIAG(J)
      AOD=A(I,J)
      ASQ=AOD*AOD
 28   IF (ASQ-AMAX) 23,23,27
 27   AMAX=ASQ
 23   IF(ASQ-EPS)11,11,12
 12   DIFFR=AII-AJJ
      IF (DIFFR) 13,15,15
 13   SIGN=-2.0
      DIFFR=-DIFFR
      GO TO 16
 15   SIGN=2.0
 16   TDEN=DIFFR+SQRT(DIFFR*DIFFR+4.0*ASQ)
      TANK=SIGN*AOD/TDEN
      C=1.0/(SQRT(1.0+TANK*TANK))
      S=C*TANK
      DO 24 K=1,N
      XJ=C*U(K,J)-S*U(K,I)
      U(K,I)=S*U(K,J)+C*U(K,I)
      U(K,J)=XJ
      IF (K-J) 17,24,18
 17   XJ=C*A(J,K)-S*A(I,K)
      A(I,K)=S*A(J,K)+C*A(I,K)
      A(J,K)=XJ
      GO TO 24
 18   IF (K-I) 19,24,21
 19   XJ=C*A(K,J)-S*A(I,K)
      A(I,K)=S*A(K,J)+C*A(I,K)
```

```
      A(K,J)=XJ
      GO TO 24
 21   XJ=C*A(K,J)-S*A(K,I)
      A(K,I)=S*A(K,J)+C*A(K,I)
      A(K,J)=XJ
 24   CONTINUE
      ADIAG(I)=C*C*AII+S*S*AJJ+2.0*S*C*AOD
      ADIAG(J)=C*C*AJJ+S*S*AII-2.0*S*C*AOD
      A(I,J)=0
 11   CONTINUE
      IF (AMAX-EPS) 20,20,10
 20   RETURN
      END
C
      SUBROUTINE SCFARR(N,A,ADIAG,U)
      DIMENSION A(30,30),ADIAG(30),U(30,30),UTEST(30)
      DO 40 K=1,N
      ATEST=ADIAG(K)
      JTEST=K
      DO 41 J=K,N
      IF (ADIAG(J)-ATEST) 42,41,41
 42   ATEST=ADIAG(J)
      JTEST=J
 41   CONTINUE
      ADIAG(JTEST)=ADIAG(K)
      ADIAG(K)=ATEST
      DO 40 I=1,N
      UTEST(I)=U(I,JTEST)
      U(I,JTEST)=U(I,K)
 40   U(I,K)=UTEST(I)
      RETURN
      END
C
      SUBROUTINE SCFNFM(N,M,MM,F,FDIAG,T,G,Z,HAFGAM)
      DIMENSION F(30,30),FDIAG(30),T(30,30),G(30,30),Z(30),DIGR(30)
      DO 11 I=1,N
      DO 11 J=1,I
      RSUM=0.
      DO 12 K=1,M
 12   RSUM=RSUM+T(I,K)*T(J,K)
      DO 13 K=M+1,M+MM
 13   RSUM=RSUM+T(I,K)*T(J,K)*0.5
      IF (J-I) 9,10,10
 9    F(I,J)=F(J,I)-RSUM*G(I,J)
      GO TO 11
 10   DIGR(I)=RSUM
 11   CONTINUE
      SUM=0.
      DO 20 J=1,N
 20   SUM=SUM+DIGR(J)
      DO 21 J=1,N
 21   DIGR(J)=(M+0.5*MM)*DIGR(J)/SUM
      DO 22 I=1,N
      RSUM=0.0
      DO 23 J=1,N
      IF (I-J) 24,23,24
 24   RSUM=RSUM+(2.0*DIGR(J)-Z(J))*G(I,J)
 23   CONTINUE
```

```
 22   FDIAG(I)=F(I,I)-HAFGAM+DIGR(I)*G(I,I)+RSUM
      RETURN
      END
C
      SUBROUTINE SCFTRF(N,F,FDIAG,T)
      DIMENSION F(30,30),FDIAG(30),T(30,30),FS(30,30)
      DO 8 I=1,N
      DO 8 J=1,N
      SUM=0.
      DO 7 K=1,N
      IF (K-I) 5,4,6
 4    SUM=SUM+FDIAG(K)*T(K,J)
      GO TO 7
 5    SUM=SUM+F(I,K)*T(K,J)
      GO TO 7
 6    SUM=SUM+F(K,I)*T(K,J)
 7    CONTINUE
 8    FS(I,J)=SUM
      DO 10 I=1,N
      DO 10 J=1,I
      SUM=0.
      DO 11 K=1,N
 11   SUM=SUM+T(K,I)*FS(K,J)
      IF (I-J) 12,13,12
 12   F(I,J)=SUM
      GO TO 10
 13   FDIAG(J)=SUM
 10   CONTINUE
      RETURN
      END
C
      SUBROUTINE SCFPIE(N,M,MM,F,T,G,Z,X,Y)
      DIMENSION X(30),Y(30)
      DIMENSION F(30,30),FDIAG(30),T(30,30),G(30,30),Z(30),R(30,30)
      DO 9 J=1,N
      DO 9 I=1,N
      SUM=0.
      DO 10 K=1,M
 10   SUM=SUM+T(I,K)*T(J,K)
      DO 13 K=M+1,M+MM
 13   SUM=SUM+0.5*T(I,K)*T(J,K)
 9    R(I,J)=SUM
      SUM=0.
      DO 20 J=1,N
 20   SUM=SUM+R(J,J)
      DO 21 J=1,N
 21   R(J,J)=(M+0.5*MM)*R(J,J)/SUM
      E=0.
      DO 8 I=1,N
      SIGK=0.
      DO 11 K=1,N
 11   SIGK=SIGK+2.0*(R(K,K)-Z(K))*G(I,K)
      DO 8 J=1,I
      BRAK=2.0*F(J,I)-R(I,J)*G(I,J)
      IF (I-J) 6,7,6
 7    TERM=SIGK+BRAK+2.0*Z(I)*G(I,I)
      GO TO 8
 6    TERM=2.0*BRAK
```

```
 8     E=E+R(I,J)*TERM
       WRITE (2,100) E
       DO 1 J=1,N
       DO 1 I=1,J
 1     R(I,J)=2*R(I,J)
       SX=0.
       SY=0.
       DO 18 I=1,N
       P=R(I,I)-Z(I)
       SX=SX+P*X(I)
 18    SY=SY+P*Y(I)
       EMU=4.77*SQRT(SX*SX+SY*SY)
       SX=4.77*SX
       SY=4.77*SY
       WRITE (2,109) EMU,SX,SY
 109   FORMAT (/15H DIPOLE MOMENT=,F8.4,2X,5H XMU=,
      *F8.4,2X,5H YMU=,F8.4)
       WRITE (2,102)
 102   FORMAT (/30H DENSITY AND BOND ORDER MATRIX)
       DO 77 J=1,N
 77    WRITE (2,101) (R(I,J),I=1,J)
 100   FORMAT (/18H BINDING ENERGY E=,F18.6)
 101   FORMAT (6(F9.5,2X))
       RETURN
       END
C
       SUBROUTINE SCFPRI(N,H,G,Z)
       DIMENSION H(30,30),G(30,30),Z(30)
       WRITE (2,100)
 100   FORMAT(//' CORE INTEGRALS')
       DO 71 J=1,N
 71    WRITE (2,103) (H(I,J),I=1,J)
 103   FORMAT(10F7.3)
       WRITE (2,101)
 101   FORMAT(/' ELECTRON REPULSION INTEGRALS')
       DO 72 I=1,N
 72    WRITE(2,103) (G(J,I),J=1,I)
       WRITE (2,102)
 102   FORMAT(/' EFFECTIVE NUCLEAR CHARGES')
       WRITE (2,103) (Z(I),I=1,N)
       RETURN
       END
C
       SUBROUTINE SCFPRN(N,FDIAG,C)
       DIMENSION FDIAG(30),C(30,30)
       WRITE (2,106)
 106   FORMAT(//' SCF LEVELS AND ORBITALS')
       DO 17 J=1,N
       WRITE (2,112) FDIAG(J)
 112   FORMAT(/,1X,' ENERGY =',F11.4/)
 17    WRITE (2,111) (C(I,J),I=1,N)
 111   FORMAT (6F10.5)
       RETURN
       END
C
       SUBROUTINE SCFHCR(N,H,G,Z)
       DIMENSION H(30,30),G(30,30),Z(30)
       DO 100 I=1,N
```

```
      RSUM=0.0
      DO 90 J=1,N
      IF (J.EQ.I) GO TO 90
      RSUM=RSUM+Z(J)*G(I,J)
90    CONTINUE
      H(I,I)=H(I,I)-RSUM
100   CONTINUE
      RETURN
      END
```

```
C  PROGRAM PPPCI
C  PROGRAM TO DO CI CALCULATION FOLLOWING PPPSCF
C  WRITTEN BY JULIANTO PRANATA, CALIFORNIA INSTITUTE OF TECHNOLOGY,
C  JANUARY 1986
C  ORIGINALLY BASED ON QCPE 314 (BUT RADICALLY MODIFIED)
      COMMON N,H,G,X,Y,C
      DIMENSION H(30,30),G(30,30),C(30,30),X(30),Y(30)
      DIMENSION II(30,500)
      DIMENSION TITLE(14)
      DIMENSION U(500,500),F(500,500),TRMX(500,500)
      DIMENSION TRMY(500,500),FDIAG(500)
      CHARACTER*7 STATE
      CALL CIDAT(EPS,TITLE,ND,NS,STATE)
      WRITE (4,1000)
 1000 FORMAT (//,' C.I. SOLUTION')
      CALL CIGEN(MINK,II,ND,NS)
      IF (STATE.EQ.'SINGLET') THEN
      CALL CIEXI1(MINK,F,FDIAG,II,TRMX,TRMY)
      ELSE IF (STATE.EQ.'TRIPLET') THEN
      CALL CIEXI3(MINK,F,FDIAG,II,TRMX,TRMY)
      ELSE
      WRITE (4,1001) STATE
 1001 FORMAT (/' UNABLE TO DO ',A7,' C.I. CALCULATION')
      GO TO 9000
      ENDIF
      NIT=0
      CALL CIPCE(MINK,II,FDIAG)
      CALL CIJAC(MINK,F,FDIAG,U,NIT,EPS)
      CALL CIARR(MINK,F,FDIAG,U)
      CALL CIPCI(MINK,F,FDIAG,U,TRMX,TRMY)
 9000 STOP
      END
C
      SUBROUTINE CIDAT(EPS,TITLE,ND,NS,STATE)
      COMMON N,H,G,X,Y,C
      DIMENSION TITLE(14),H(30,30),G(30,30),C(30,30),X(30),Y(30)
      CHARACTER*7 STATE
      READ (3,103) (TITLE(I),I=1,14)
 103  FORMAT(14A4)
      READ (3,99) STATE
 99   FORMAT (A7)
      EPS=1.0E-16
      READ (3,104) N,ND,NS
 104  FORMAT(3I3)
      WRITE (4,105) TITLE
 105  FORMAT (//,5X,14A4)
      WRITE (4,98) STATE
 98   FORMAT (/,5X,A7,' C.I. CALCULATION')
 200  FORMAT (6F12.8)
      DO 20 I=1,N
 20   READ (3,200) (H(I,J),J=1,N)
      DO 30 I=1,N
 30   READ (3,200) (G(I,J),J=1,N)
      DO 40 I=1,N
 40   READ (3,200) (C(I,J),J=1,N)
      READ (3,200) (X(I),I=1,N)
      READ (3,200) (Y(I),I=1,N)
 110  FORMAT (/' CORE INTEGRALS')
```

```
 111  FORMAT (/' ELECTRON REPULSION INTEGRALS')
 112  FORMAT (//' SCF MOLECULAR ORBITALS')
 113  FORMAT (/' ORBITAL NO.',I4)
 114  FORMAT (/' NUCLEAR COORDINATES')
 115  FORMAT ('    X =',6F8.3)
 116  FORMAT ('    Y =',6F8.3)
 117  FORMAT (6F10.5)
      WRITE (4,114)
      WRITE (4,115) (X(I),I=1,N)
      WRITE (4,116) (Y(I),I=1,N)
      WRITE (4,110)
      DO 120 I=1,N
 120  WRITE (4,117) (H(I,J),J=1,I)
      WRITE (4,111)
      DO 130 I=1,N
 130  WRITE (4,117) (G(I,J),J=1,I)
      WRITE (4,112)
      DO 140 I=1,N
      WRITE (4,113) I
 140  WRITE (4,117) (C(J,I),J=1,N)
      RETURN
      END
C
      SUBROUTINE CIJAC(N,A,ADIAG,U,NIT,EPS)
      DIMENSION A(500,500),U(500,500),ADIAG(500)
      IF (NIT) 10,999,10
 999  DO 8 J=1,N
      DO 9 I=1,N
 9    U(I,J)=0.0
 8    U(J,J)=1.0
 10   AMAX=0.0
      DO 11 I=2,N
      JUP = I-1
      DO 11 J=1,JUP
      AII=ADIAG(I)
      AJJ=ADIAG(J)
      AOD=A(I,J)
      ASQ=AOD*AOD
 28   IF (ASQ-AMAX) 23,23,27
 27   AMAX=ASQ
 23   IF(ASQ-EPS)11,11,12
 12   DIFFR=AII-AJJ
      IF (DIFFR) 13,15,15
 13   SIGN=-2.0
      DIFFR=-DIFFR
      GO TO 16
 15   SIGN=2.0
 16   TDEN=DIFFR+SQRT(DIFFR*DIFFR+4.0*ASQ)
      TANK=SIGN*AOD/TDEN
      C=1.0/(SQRT(1.0+TANK*TANK))
      S=C*TANK
      DO 24 K=1,N
      XJ=C*U(K,J)-S*U(K,I)
      U(K,I)=S*U(K,J)+C*U(K,I)
      U(K,J)=XJ
      IF (K-J) 17,24,18
 17   XJ=C*A(J,K)-S*A(I,K)
      A(I,K)=S*A(J,K)+C*A(I,K)
```

```
      A(J,K)=XJ
      GO TO 24
 18   IF (K-I) 19,24,21
 19   XJ=C*A(K,J)-S*A(I,K)
      A(I,K)=S*A(K,J)+C*A(I,K)
      A(K,J)=XJ
      GO TO 24
 21   XJ=C*A(K,J)-S*A(K,I)
      A(K,I)=S*A(K,J)+C*A(K,I)
      A(K,J)=XJ
 24   CONTINUE
      ADIAG(I)=C*C*AII+S*S*AJJ+2.0*S*C*AOD
      ADIAG(J)=C*C*AJJ+S*S*AII-2.0*S*C*AOD
      A(I,J)=0
 11   CONTINUE
      IF (AMAX-EPS) 20,20,10
 20   RETURN
      END
C
      SUBROUTINE CIARR(N,A,ADIAG,U)
      DIMENSION A(500,500),ADIAG(500),U(500,500),UTEST(500)
      DO 40 K=1,N
      ATEST=ADIAG(K)
      JTEST=K
      DO 41 J=K,N
      IF (ADIAG(J)-ATEST) 42,41,41
 42   ATEST=ADIAG(J)
      JTEST=J
 41   CONTINUE
      ADIAG(JTEST)=ADIAG(K)
      ADIAG(K)=ATEST
      DO 40 I=1,N
      UTEST(I)=U(I,JTEST)
      U(I,JTEST)=U(I,K)
 40   U(I,K)=UTEST(I)
      RETURN
      END
C
      SUBROUTINE CIPCE(MINK,II,D)
      COMMON N,H,G,X,Y,C
      DIMENSION H(30,30),G(30,30),C(30,30),X(30),Y(30)
      DIMENSION D(500),II(30,500)
      READ (3,100) IOPT
 100  FORMAT (I2)
      IF (IOPT.EQ.0) GO TO 900
      WRITE (4,101)
 101  FORMAT (//' SCF CONFIGURATION ENERGIES',
     *//'   ENERGY    CONFIGURATION',/)
      DO 10 I=1,MINK
      WRITE (4,102) D(I),(II(J,I),J=1,N)
 10   CONTINUE
 102  FORMAT (F10.4,3X,30I1)
 900  RETURN
      END
C
      SUBROUTINE CIPCI(MINK,H,HDIAG,C,TRMX,TRMY)
      DIMENSION TRMX(500,500),TRMY(500,500),OSC(500)
      DIMENSION H(500,500),HDIAG(500)
```

```
      DIMENSION C(500,500)
      DIMENSION TRX(500),TRY(500),ALAM(500)
      READ (3,1) IOPT,NSTATE
 1    FORMAT (2I2)
      IF (NSTATE.EQ.0) NSTATE=MINK
      WRITE(4,105)
 105  FORMAT (/' C.I. STATES')
      IF (IOPT.EQ.0) GO TO 3000
      DO 9 J=1,NSTATE
      WRITE (4,1001) HDIAG(J)
 1001 FORMAT (/10H ENERGY = ,F13.6,/)
      WRITE (4,1009) (C(I,J),I=1,MINK)
 1009 FORMAT (10(1X,F6.4))
 9    CONTINUE
 3000 DO 11 J=2,NSTATE
      SX=0
      SY=0
      DO 10 I=1,MINK
      DO 10 K=1,MINK
      SX=SX+C(I,1)*C(K,J)*TRMX(I,K)
 10   SY=SY+C(I,1)*C(K,J)*TRMY(I,K)
      TRX(J)=SX
      TRY(J)=SY
 11   OSC(J)=0.087379*(SX*SX+SY*SY)*(HDIAG(J)-HDIAG(1))
      DO 800,J=2,NSTATE
      ALAM(J)=0.1241712E+04/(HDIAG(J)-HDIAG(1))
 800  CONTINUE
      WRITE (4,1003)
 1003 FORMAT (/' TRANSITION WAVELENGTHS AND OSCILLATOR - STRENGTHS')
      WRITE (4,1004)
 1004 FORMAT (/2X,6HENERGY,8X,14HWAVELENGTH(NM),4X,11HX-COMPONENT,
     *3X,11HY-COMPONENT,2X,10HOSCILLATOR)
      WRITE (4,2000)
 2000 FORMAT (62X,8HSTRENGTH)
      DO 1005 J=2,NSTATE
      HDIAG(J)=HDIAG(J)-HDIAG(1)
      WRITE (4,1006) HDIAG(J),ALAM(J),TRX(J),TRY(J),OSC(J)
 1006 FORMAT (/,F13.6,1X,F13.6,4X,F11.3,3X,F11.3,2X,F11.3)
 1005 CONTINUE
      RETURN
      END
C
      REAL FUNCTION HCORE(I,J)
      COMMON N,H,G,X,Y,C
      DIMENSION C(30,30),H(30,30),G(30,30),X(30),Y(30)
      HCORE=0.0
      DO 10 MU=1,N
      DO 10 NU=1,N
 10   HCORE=HCORE+C(MU,I)*C(NU,J)*H(MU,NU)
      RETURN
      END
C
      REAL FUNCTION GAMMA(I,J,K,L)
      COMMON N,H,G,X,Y,C
      DIMENSION C(30,30),H(30,30),G(30,30),X(30),Y(30)
      GAMMA=0.0
      DO 10 MU=1,N
      DO 10 NU=1,N
```

```
 10   GAMMA=GAMMA+C(MU,I)*C(MU,J)*C(NU,K)*C(NU,L)*G(MU,NU)
      RETURN
      END
C
      REAL FUNCTION TMX(I,J)
      COMMON N,H,G,X,Y,C
      DIMENSION C(30,30),H(30,30),G(30,30),X(30),Y(30)
      TMX=0.0
      DO 10 MU=1,N
 10   TMX=TMX+C(MU,I)*C(MU,J)*X(MU)
      RETURN
      END
C
      REAL FUNCTION TMY(I,J)
      COMMON N,H,G,X,Y,C
      DIMENSION C(30,30),H(30,30),G(30,30),X(30),Y(30)
      TMY=0.0
      DO 10 MU=1,N
 10   TMY=TMY+C(MU,I)*C(MU,J)*Y(MU)
      RETURN
      END
C
      SUBROUTINE CIGEN(MINK,II,ND,NS)
      COMMON N,H,G,X,Y,C
      DIMENSION H(30,30),G(30,30),C(30,30),X(30),Y(30)
      DIMENSION II(30,500),NEL(30)
      READ (3,10) IOPT
 10   FORMAT (I2)
      IF (IOPT.EQ.0) WRITE (4,2000)
      IF (IOPT.EQ.1) WRITE (4,2001)
      IF (IOPT.EQ.2) WRITE (4,2002)
      IF (IOPT.EQ.3) WRITE (4,2003)
      IF (IOPT.EQ.4) WRITE (4,2004)
      IF (IOPT.EQ.5) WRITE (4,2005)
 2000 FORMAT (/' USER SPECIFIED CONFIGURATIONS')
 2001 FORMAT (/' EXCITATIONS WITHIN NBMOS ONLY')
 2002 FORMAT (/' SINGLE EXCITATIONS TO AND FROM NBMOS')
 2003 FORMAT (/' SINGLE AND DOUBLE EXCITATIONS TO AND FROM NBMOS')
 2004 FORMAT (/' SINGLE EXCITATIONS')
 2005 FORMAT (/' SINGLE AND DOUBLE EXCITATIONS')
C  USER SPECIFIED CONFIGURATIONS
      IF (IOPT.NE.0) GO TO 20
      READ (3,11) MINK
      DO 13 I=1,MINK
 13   READ (3,12) (II(J,I),J=1,N)
 11   FORMAT (I4)
 12   FORMAT (30I2)
      GO TO 901
 20   READ (3,10) LVLS
      WRITE (4,2006) LVLS
 2006 FORMAT (' LEVEL OF EXCITATIONS:',I6)
C  DEFAULT OCCUPATIONS
      M=N/2
      NORB=N
      DO 21 I=1,M
      NEL(I)=2
 21   NEL(M+I)=0
      ICNT=0
```

```
      NOEL=0
      CALL NBMOE(NORB,ND,NS,NOEL,II,NEL,ICNT)
      IF (NS.EQ.0) GO TO 30
      IF (IOPT.EQ.1) GO TO 900
      LVL=1
      NHOLE=1
      NELEC=0
      NOEL=1
      CALL BMO(LVLS,NORB,ND,NS,LVL,NHOLE,NELEC,NOEL,II,NEL,ICNT)
      NELEC=1
      NOEL=-1
      CALL ABMO(LVLS,NORB,ND,NS,NELEC,NOEL,II,NEL,ICNT)
      IF (IOPT.EQ.2) GO TO 900
      IF (IOPT.EQ.4) GO TO 30
      LVL=1
      NHOLE=2
      NELEC=0
      NOEL=2
      CALL BMO(LVLS,NORB,ND,NS,LVL,NHOLE,NELEC,NOEL,II,NEL,ICNT)
      NELEC=2
      NOEL=-2
      CALL ABMO(LVLS,NORB,ND,NS,NELEC,NOEL,II,NEL,ICNT)
      IF (IOPT.EQ.3) GO TO 900
 30   LVL=2
      NHOLE=1
      NELEC=1
      NOEL=0
      CALL BMO(LVLS,NORB,ND,NS,LVL,NHOLE,NELEC,NOEL,II,NEL,ICNT)
      IF (IOPT.EQ.4) GO TO 900
      LVL=2
      NHOLE=2
      NELEC=2
      NOEL=0
      CALL BMO(LVLS,NORB,ND,NS,LVL,NHOLE,NELEC,NOEL,II,NEL,ICNT)
      IF (NS.EQ.0) GO TO 900
      NHOLE=2
      NELEC=1
      NOEL=1
      CALL BMO(LVLS,NORB,ND,NS,LVL,NHOLE,NELEC,NOEL,II,NEL,ICNT)
      NHOLE=1
      NELEC=2
      NOEL=-1
      CALL BMO(LVLS,NORB,ND,NS,LVL,NHOLE,NELEC,NOEL,II,NEL,ICNT)
 900  MINK=ICNT
 901  CONTINUE
C  OUTPUT
C       DO 1900 I=1,MINK
C 1900 WRITE (4,1901) (II(J,I),J=1,N)
C 1901 FORMAT (5X,30I2)
      RETURN
      END
C
      SUBROUTINE BMO(LVLS,N,ND,NS,LVL,NHOLE,NELEC,NOEL,II,NEL,ICNT)
      DIMENSION II(30,500),NEL(30)
      DO 30 I=ND,ND-LVLS+1,-1
      NEL(I)=NEL(I)-1
      IF (NHOLE.EQ.1) GO TO 10
      DO 31 J=I,ND-LVLS+1,-1
```

```
      NEL(J)=NEL(J)-1
 10   IF (LVL.EQ.2) GO TO 20
      IF (MOD(ABS(NOEL),2).EQ.1) CALL NBMOD(N,ND,NS,NOEL,II,NEL,ICNT)
      IF (MOD(ABS(NOEL),2).EQ.0) CALL NBMOE(N,ND,NS,NOEL,II,NEL,ICNT)
      GO TO 21
 20   CALL ABMO(LVLS,N,ND,NS,NELEC,NOEL,II,NEL,ICNT)
 21   IF (NHOLE.EQ.1) GO TO 30
 31   NEL(J)=NEL(J)+1
 30   NEL(I)=NEL(I)+1
      RETURN
      END
C
      SUBROUTINE ABMO(LVLS,N,ND,NS,NELEC,NOEL,II,NEL,ICNT)
      DIMENSION II(30,500),NEL(30)
      LOW=ND+NS+1
      DO 50 I=LOW,LOW+LVLS-1
      NEL(I)=NEL(I)+1
      IF (NELEC.EQ.1) GO TO 10
      DO 51 J=I,LOW+LVLS-1
      NEL(J)=NEL(J)+1
 10   IF (MOD(ABS(NOEL),2).EQ.1) CALL NBMOD(N,ND,NS,NOEL,II,NEL,ICNT)
      IF (MOD(ABS(NOEL),2).EQ.0) CALL NBMOE(N,ND,NS,NOEL,II,NEL,ICNT)
      IF (NELEC.EQ.1) GO TO 50
 51   NEL(J)=NEL(J)-1
 50   NEL(I)=NEL(I)-1
      RETURN
      END
C
      SUBROUTINE NBMOE(N,ND,NS,NOEL,NL1,NEL,ICNT)
      DIMENSION NL1(30,500),NEL(30)
      IF (NS.EQ.0) GO TO 3
      LL=ND+1
      LU=ND+NS
      LM=ND+NS/2+NOEL/2
      LN=LM+1
C     NON-EXCITED CONFIGURATION
      IF (NOEL.EQ.2) NEL(LM)=NEL(LM)+2
      IF (NOEL.EQ.-2) NEL(LN)=NEL(LN)-2
 3    ICNT=ICNT+1
      DO 1 I=1,N
 1    NL1(I,ICNT)=NEL(I)
      IF (NS.EQ.0) GO TO 19
      IF ((NS-ABS(NOEL)).EQ.0) GO TO 19
C    SINGLY EXCITED CONFIGURATIONS
      DO 60 IX=LM,LL,-1
      NEL(IX)=NEL(IX)-1
      DO 61 JX=LN,LU
      NEL(JX)=NEL(JX)+1
      ICNT=ICNT+1
      DO 62 MM=1,N
 62   NL1(MM,ICNT)=NEL(MM)
 61   NEL(JX)=NEL(JX)-1
 60   NEL(IX)=NEL(IX)+1
C    DOUBLY EXCITED CONFIGURATIONS
      DO 70 IX=LM,LL,-1
      NEL(IX)=NEL(IX)-1
      DO 71 IY=IX,LL,-1
      NEL(IY)=NEL(IY)-1
```

```
      DO 72 JX=LN,LU
      NEL(JX)=NEL(JX)+1
      DO 73 JY=JX,LU
      NEL(JY)=NEL(JY)+1
      ICNT=ICNT+1
      DO 74 MM=1,N
 74   NL1(MM,ICNT)=NEL(MM)
 73   NEL(JY)=NEL(JY)-1
 72   NEL(JX)=NEL(JX)-1
 71   NEL(IY)=NEL(IY)+1
 70   NEL(IX)=NEL(IX)+1
      IF ((NS-ABS(NOEL)).EQ.2) GO TO 19
C   TRIPLY EXCITED CONFIGURATIONS
      DO 80 IX=LM,LL,-1
      NEL(IX)=NEL(IX)-1
      DO 81 IY=IX,LL,-1
      NEL(IY)=NEL(IY)-1
      DO 82 IZ=IY,LL,-1
      NEL(IZ)=NEL(IZ)-1
      IF (NEL(IZ).LT.0) GO TO 82
      DO 83 JX=LN,LU
      NEL(JX)=NEL(JX)+1
      DO 84 JY=JX,LU
      NEL(JY)=NEL(JY)+1
      DO 85 JZ=JY,LU
      NEL(JZ)=NEL(JZ)+1
      IF (NEL(JZ).GT.2) GO TO 85
      ICNT=ICNT+1
      DO 86 MM=1,N
 86   NL1(MM,ICNT)=NEL(MM)
 85   NEL(JZ)=NEL(JZ)-1
 84   NEL(JY)=NEL(JY)-1
 83   NEL(JX)=NEL(JX)-1
 82   NEL(IZ)=NEL(IZ)+1
 81   NEL(IY)=NEL(IY)+1
 80   NEL(IX)=NEL(IX)+1
C   QUADRUPLY EXCITED CONFIGURATIONS
      DO 90 IX=LM,LL,-1
      NEL(IX)=NEL(IX)-1
      DO 91 IY=IX,LL,-1
      NEL(IY)=NEL(IY)-1
      DO 92 IZ=IY,LL,-1
      NEL(IZ)=NEL(IZ)-1
      IF (NEL(IZ).LT.0) GO TO 92
      DO 93 IW=IZ,LL,-1
      NEL(IW)=NEL(IW)-1
      IF (NEL(IW).LT.0) GO TO 93
      DO 94 JX=LN,LU
      NEL(JX)=NEL(JX)+1
      DO 95 JY=JX,LU
      NEL(JY)=NEL(JY)+1
      DO 96 JZ=JY,LU
      NEL(JZ)=NEL(JZ)+1
      IF (NEL(JZ).GT.2) GO TO 96
      DO 97 JW=JZ,LU
      NEL(JW)=NEL(JW)+1
      IF (NEL(JW).GT.2) GO TO 97
      ICNT=ICNT+1
```

```
      DO 98 MM=1,N
 98   NL1(MM,ICNT)=NEL(MM)
 97   NEL(JW)=NEL(JW)-1
 96   NEL(JZ)=NEL(JZ)-1
 95   NEL(JY)=NEL(JY)-1
 94   NEL(JX)=NEL(JX)-1
 93   NEL(IW)=NEL(IW)+1
 92   NEL(IZ)=NEL(IZ)+1
 91   NEL(IY)=NEL(IY)+1
 90   NEL(IX)=NEL(IX)+1
      IF ((NS-ABS(NOEL)).EQ.4) GO TO 19
C   QUINTUPLY EXCITED CONFIGURATIONS
      DO 100 IX=LM,LL,-1
      NEL(IX)=NEL(IX)-1
      DO 101 IY=IX,LL,-1
      NEL(IY)=NEL(IY)-1
      DO 102 IZ=IY,LL,-1
      NEL(IZ)=NEL(IZ)-1
      IF (NEL(IZ).LT.0) GO TO 102
      DO 103 IW=IZ,LL,-1
      NEL(IW)=NEL(IW)-1
      IF (NEL(IW).LT.0) GO TO 103
      DO 104 IV=IW,LL,-1
      NEL(IV)=NEL(IV)-1
      IF (NEL(IV).LT.0) GO TO 104
      DO 105 JX=LN,LU
      NEL(JX)=NEL(JX)+1
      DO 106 JY=JX,LU
      NEL(JY)=NEL(JY)+1
      DO 107 JZ=JY,LU
      NEL(JZ)=NEL(JZ)+1
      IF (NEL(JZ).GT.2) GO TO 107
      DO 108 JW=JZ,LU
      NEL(JW)=NEL(JW)+1
      IF (NEL(JW).GT.2) GO TO 108
      DO 109 JV=JW,LU
      NEL(JV)=NEL(JV)+1
      IF (NEL(JV).GT.2) GO TO 109
      ICNT=ICNT+1
      DO 110 MM=1,N
110   NL1(MM,ICNT)=NEL(MM)
109   NEL(JV)=NEL(JV)-1
108   NEL(JW)=NEL(JW)-1
107   NEL(JZ)=NEL(JZ)-1
106   NEL(JY)=NEL(JY)-1
105   NEL(JX)=NEL(JX)-1
104   NEL(IV)=NEL(IV)+1
103   NEL(IW)=NEL(IW)+1
102   NEL(IZ)=NEL(IZ)+1
101   NEL(IY)=NEL(IY)+1
100   NEL(IX)=NEL(IX)+1
C   SEXTUPLY EXCITED CONFIGURATIONS
      DO 120 IX=LM,LL,-1
      NEL(IX)=NEL(IX)-1
      DO 121 IY=IX,LL,-1
      NEL(IY)=NEL(IY)-1
      DO 122 IZ=IY,LL,-1
      NEL(IZ)=NEL(IZ)-1
```

```
      IF (NEL(IZ).LT.0) GO TO 122
      DO 123 IW=IZ,LL,-1
      NEL(IW)=NEL(IW)-1
      IF (NEL(IW).LT.0) GO TO 123
      DO 124 IV=IW,LL,-1
      NEL(IV)=NEL(IV)-1
      IF (NEL(IV).LT.0) GO TO 124
      DO 125 IU=IV,LL,-1
      NEL(IU)=NEL(IU)-1
      IF (NEL(IU).LT.0) GO TO 125
      DO 126 JX=LN,LU
      NEL(JX)=NEL(JX)+1
      DO 127 JY=JX,LU
      NEL(JY)=NEL(JY)+1
      DO 128 JZ=JY,LU
      NEL(JZ)=NEL(JZ)+1
      IF (NEL(JZ).GT.2) GO TO 128
      DO 129 JW=JZ,LU
      NEL(JW)=NEL(JW)+1
      IF (NEL(JW).GT.2) GO TO 129
      DO 130 JV=JW,LU
      NEL(JV)=NEL(JV)+1
      IF (NEL(JV).GT.2) GO TO 130
      DO 131 JU=JV,LU
      NEL(JU)=NEL(JU)+1
      IF (NEL(JU).GT.2) GO TO 131
      ICNT=ICNT+1
      DO 132 MM=1,N
 132  NL1(MM,ICNT)=NEL(MM)
 131  NEL(JU)=NEL(JU)-1
 130  NEL(JV)=NEL(JV)-1
 129  NEL(JW)=NEL(JW)-1
 128  NEL(JZ)=NEL(JZ)-1
 127  NEL(JY)=NEL(JY)-1
 126  NEL(JX)=NEL(JX)-1
 125  NEL(IU)=NEL(IU)+1
 124  NEL(IV)=NEL(IV)+1
 123  NEL(IW)=NEL(IW)+1
 122  NEL(IZ)=NEL(IZ)+1
 121  NEL(IY)=NEL(IY)+1
 120  NEL(IX)=NEL(IX)+1
 19   IF (NOEL.EQ.2) NEL(LM)=NEL(LM)-2
      IF (NOEL.EQ.-2) NEL(LN)=NEL(LN)+2
      RETURN
      END
C
      SUBROUTINE NBMOD(N,ND,NS,NOEL,NL1,NEL,ICNT)
      DIMENSION NL1(30,500),NEL(30)
      LL=ND+1
      LU=ND+NS
      LM=ND+NS/2+(NOEL+1)/2
C   NON-EXCITED CONFIGURATION
      IF (NOEL.EQ.-1) NEL(LM)=NEL(LM)-1
      IF (NOEL.EQ.1) NEL(LM)=NEL(LM)+1
      ICNT=ICNT+1
      DO 300 I=1,N
300   NL1(I,ICNT)=NEL(I)
C   SINGLY EXCITED CONFIGURATIONS
```

```
      NEL(LM)=NEL(LM)-1
      DO 310 JX=LM+1,LU
      NEL(JX)=NEL(JX)+1
      ICNT=ICNT+1
      DO 311 MM=1,N
 311  NL1(MM,ICNT)=NEL(MM)
 310  NEL(JX)=NEL(JX)-1
      NEL(LM)=NEL(LM)+1
      IF (LM.EQ.LL) GO TO 315
      DO 312 IX=LM-1,LL,-1
      NEL(IX)=NEL(IX)-1
      DO 313 JX=LM,LU
      NEL(JX)=NEL(JX)+1
      ICNT=ICNT+1
      DO 314 MM=1,N
 314  NL1(MM,ICNT)=NEL(MM)
 313  NEL(JX)=NEL(JX)-1
 312  NEL(IX)=NEL(IX)+1
 315  IF (NS.EQ.2) GO TO 16
C   DOUBLY EXCITED CONFIGURATIONS
      NEL(LM)=NEL(LM)-1
      DO 320 IY=LM-1,LL,-1
      NEL(IY)=NEL(IY)-1
      DO 321 JX=LM+1,LU
      NEL(JX)=NEL(JX)+1
      DO 322 JY=JX,LU
      NEL(JY)=NEL(JY)+1
      ICNT=ICNT+1
      DO 323 MM=1,N
 323  NL1(MM,ICNT)=NEL(MM)
 322  NEL(JY)=NEL(JY)-1
 321  NEL(JX)=NEL(JX)-1
 320  NEL(IY)=NEL(IY)+1
      NEL(LM)=NEL(LM)+1
      DO 324 IX=LM-1,LL,-1
      NEL(IX)=NEL(IX)-1
      DO 325 IY=IX,LL,-1
      NEL(IY)=NEL(IY)-1
      DO 326 JX=LM,LU
      NEL(JX)=NEL(JX)+1
      DO 327 JY=JX,LU
      NEL(JY)=NEL(JY)+1
      IF (NEL(JY).GT.2) GO TO 327
      ICNT=ICNT+1
      DO 328 MM=1,N
 328  NL1(MM,ICNT)=NEL(MM)
 327  NEL(JY)=NEL(JY)-1
 326  NEL(JX)=NEL(JX)-1
 325  NEL(IY)=NEL(IY)+1
 324  NEL(IX)=NEL(IX)+1
C   TRIPLY EXCITED CONFIGURATIONS
      NEL(LM)=NEL(LM)-1
      DO 330 IY=LM-1,LL,-1
      NEL(IY)=NEL(IY)-1
      DO 331 IZ=IY,LL,-1
      NEL(IZ)=NEL(IZ)-1
      DO 332 JX=LM+1,LU
      NEL(JX)=NEL(JX)+1
```

```
      DO 333 JY=JX,LU
      NEL(JY)=NEL(JY)+1
      DO 334 JZ=JY,LU
      NEL(JZ)=NEL(JZ)+1
      IF (NEL(JZ).GT.2) GO TO 334
      ICNT=ICNT+1
      DO 335 MM=1,N
  335 NL1(MM,ICNT)=NEL(MM)
  334 NEL(JZ)=NEL(JZ)-1
  333 NEL(JY)=NEL(JY)-1
  332 NEL(JX)=NEL(JX)-1
  331 NEL(IZ)=NEL(IZ)+1
  330 NEL(IY)=NEL(IY)+1
      NEL(LM)=NEL(LM)+1
      DO 336 IX=LM-1,LL,-1
      NEL(IX)=NEL(IX)-1
      DO 337 IY=IX,LL,-1
      NEL(IY)=NEL(IY)-1
      DO 338 IZ=IY,LL,-1
      NEL(IZ)=NEL(IZ)-1
      IF (NEL(IZ).LT.0) GO TO 338
      DO 339 JX=LM,LU
      NEL(JX)=NEL(JX)+1
      DO 340 JY=JX,LU
      NEL(JY)=NEL(JY)+1
      IF (NEL(JY).GT.2) GO TO 340
      DO 341 JZ=JY,LU
      NEL(JZ)=NEL(JZ)+1
      IF (NEL(JZ).GT.2) GO TO 341
      ICNT=ICNT+1
      DO 342 MM=1,N
  342 NL1(MM,ICNT)=NEL(MM)
  341 NEL(JZ)=NEL(JZ)-1
  340 NEL(JY)=NEL(JY)-1
  339 NEL(JX)=NEL(JX)-1
  338 NEL(IZ)=NEL(IZ)+1
  337 NEL(IY)=NEL(IY)+1
  336 NEL(IX)=NEL(IX)+1
      IF (NS.EQ.4) GO TO 16
C   QUADRUPLY EXCITED CONFIGURATIONS
      NEL(LM)=NEL(LM)-1
      DO 350 IY=LM-1,LL,-1
      NEL(IY)=NEL(IY)-1
      DO 351 IZ=IY,LL,-1
      NEL(IZ)=NEL(IZ)-1
      DO 352 IW=IZ,LL,-1
      NEL(IW)=NEL(IW)-1
      IF (NEL(IW).LT.0) GO TO 352
      DO 353 JX=LM+1,LU
      NEL(JX)=NEL(JX)+1
      DO 354 JY=JX,LU
      NEL(JY)=NEL(JY)+1
      DO 355 JZ=JY,LU
      NEL(JZ)=NEL(JZ)+1
      IF (NEL(JZ).GT.2) GO TO 355
      DO 356 JW=JZ,LU
      NEL(JW)=NEL(JW)+1
      IF (NEL(JW).GT.2) GO TO 356
```

```
      ICNT=ICNT+1
      DO 357 MM=1,N
  357 NL1(MM,ICNT)=NEL(MM)
  356 NEL(JW)=NEL(JW)-1
  355 NEL(JZ)=NEL(JZ)-1
  354 NEL(JY)=NEL(JY)-1
  353 NEL(JX)=NEL(JX)-1
  352 NEL(IW)=NEL(IW)+1
  351 NEL(IZ)=NEL(IZ)+1
  350 NEL(IY)=NEL(IY)+1
      NEL(LM)=NEL(LM)+1
      DO 358 IX=LM-1,LL,-1
      NEL(IX)=NEL(IX)-1
      DO 359 IY=IX,LL,-1
      NEL(IY)=NEL(IY)-1
      DO 360 IZ=IY,LL,-1
      NEL(IZ)=NEL(IZ)-1
      IF (NEL(IZ).LT.0) GO TO 360
      DO 361 IW=IZ,LL,-1
      NEL(IW)=NEL(IW)-1
      IF (NEL(IW).LT.0) GO TO 361
      DO 362 JX=LM,LU
      NEL(JX)=NEL(JX)+1
      DO 363 JY=JX,LU
      NEL(JY)=NEL(JY)+1
      IF (NEL(JY).GT.2) GO TO 363
      DO 364 JZ=JY,LU
      NEL(JZ)=NEL(JZ)+1
      IF (NEL(JZ).GT.2) GO TO 364
      DO 365 JW=JZ,LU
      NEL(JW)=NEL(JW)+1
      IF (NEL(JW).GT.2) GO TO 365
      ICNT=ICNT+1
      DO 366 MM=1,N
  366 NL1(MM,ICNT)=NEL(MM)
  365 NEL(JW)=NEL(JW)-1
  364 NEL(JZ)=NEL(JZ)-1
  363 NEL(JY)=NEL(JY)-1
  362 NEL(JX)=NEL(JX)-1
  361 NEL(IW)=NEL(IW)+1
  360 NEL(IZ)=NEL(IZ)+1
  359 NEL(IY)=NEL(IY)+1
  358 NEL(IX)=NEL(IX)+1
C   QUINTUPLY EXCITED CONFIGURATIONS
      NEL(LM)=NEL(LM)-1
      DO 370 IY=LM-1,LL,-1
      NEL(IY)=NEL(IY)-1
      DO 371 IZ=IY,LL,-1
      NEL(IZ)=NEL(IZ)-1
      DO 372 IW=IZ,LL,-1
      NEL(IW)=NEL(IW)-1
      IF (NEL(IW).LT.0) GO TO 372
      DO 373 IV=IW,LL,-1
      NEL(IV)=NEL(IV)-1
      IF (NEL(IV).LT.0) GO TO 373
      DO 374 JX=LM+1,LU
      NEL(JX)=NEL(JX)+1
      DO 375 JY=JX,LU
```

```
      NEL(JY)=NEL(JY)+1
      DO 376 JZ=JY,LU
      NEL(JZ)=NEL(JZ)+1
      IF (NEL(JZ).GT.2) GO TO 376
      DO 377 JW=JZ,LU
      NEL(JW)=NEL(JW)+1
      IF (NEL(JW).GT.2) GO TO 377
      DO 378 JV=JW,LU
      NEL(JV)=NEL(JV)+1
      IF (NEL(JV).GT.2) GO TO 378
      ICNT=ICNT+1
      DO 379 MM=1,N
379   NL1(MM,ICNT)=NEL(MM)
378   NEL(JV)=NEL(JV)-1
377   NEL(JW)=NEL(JW)-1
376   NEL(JZ)=NEL(JZ)-1
375   NEL(JY)=NEL(JY)-1
374   NEL(JX)=NEL(JX)-1
373   NEL(IV)=NEL(IV)+1
372   NEL(IW)=NEL(IW)+1
371   NEL(IZ)=NEL(IZ)+1
370   NEL(IY)=NEL(IY)+1
      NEL(LM)=NEL(LM)+1
      DO 380 IX=LM-1,LL,-1
      NEL(IX)=NEL(IX)-1
      DO 381 IY=IX,LL,-1
      NEL(IY)=NEL(IY)-1
      DO 382 IZ=IY,LL,-1
      NEL(IZ)=NEL(IZ)-1
      IF (NEL(IZ).LT.0) GO TO 382
      DO 383 IW=IZ,LL,-1
      NEL(IW)=NEL(IW)-1
      IF (NEL(IW).LT.0) GO TO 383
      DO 384 IV=IW,LL,-1
      NEL(IV)=NEL(IV)-1
      IF (NEL(IV).LT.0) GO TO 384
      DO 385 JX=LM,LU
      NEL(JX)=NEL(JX)+1
      DO 386 JY=JX,LU
      NEL(JY)=NEL(JY)+1
      IF (NEL(JY).GT.2) GO TO 386
      DO 387 JZ=JY,LU
      NEL(JZ)=NEL(JZ)+1
      IF (NEL(JZ).GT.2) GO TO 387
      DO 388 JW=JZ,LU
      NEL(JW)=NEL(JW)+1
      IF (NEL(JW).GT.2) GO TO 388
      DO 389 JV=JW,LU
      NEL(JV)=NEL(JV)+1
      IF (NEL(JV).GT.2) GO TO 389
      ICNT=ICNT+1
      DO 390 MM=1,N
390   NL1(MM,ICNT)=NEL(MM)
389   NEL(JV)=NEL(JV)-1
388   NEL(JW)=NEL(JW)-1
387   NEL(JZ)=NEL(JZ)-1
386   NEL(JY)=NEL(JY)-1
385   NEL(JX)=NEL(JX)-1
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```
 384   NEL(IV)=NEL(IV)+1
 383   NEL(IW)=NEL(IW)+1
 382   NEL(IZ)=NEL(IZ)+1
 381   NEL(IY)=NEL(IY)+1
 380   NEL(IX)=NEL(IX)+1
 16    IF (NOEL.EQ.-1) NEL(LM)=NEL(LM)+1
       IF (NOEL.EQ.1) NEL(LM)=NEL(LM)-1
       RETURN
       END
C
       SUBROUTINE CIEXI1(MINK,F,FDIAG,II,TRMX,TRMY)
       COMMON N,H,G,X,Y,C
       DIMENSION H(30,30),G(30,30),C(30,30),X(30),Y(30)
       DIMENSION II(30,500),F(500,500),FDIAG(500),TRMX(500,500)
       DIMENSION TRMY(500,500),IIN(30,500)
       DIMENSION R(3,3),TX(3,3),TY(3,3)
       INTEGER SS(4),DS(4),SD(4),SE(4),ES(4),DE,ED
C       INTEGER DD(15)
C       CHARACTER*4 CODE
       MNK=2*MINK
       DO 950 I=1,MNK
       DO 950 J=1,MNK
       F(I,J)=0.0
       TRMY(I,J)=0.0
 950   TRMX(I,J)=0.0
       IN=1
       DO 901 I=1,MINK
       JN=1
       DO 900 J=1,I
       DO 10 K=1,3
       DO 10 L=1,3
       R(K,L)=0.0
       TX(K,L)=0.0
 10    TY(K,L)=0.0
C       NDD=0
       NSS=0
       NDS=0
       NSD=0
       NSE=0
       NES=0
       NDE=0
       NED=0
C   IDENTIFY OCCUPATION PATTERNS
       DO 11 IJ=1,N
       IF (II(IJ,I).NE.2) GO TO 12
       IF (II(IJ,J).NE.2) GO TO 13
C       NDD=NDD+1
C       DD(NDD)=IJ
       GO TO 11
 13    IF (II(IJ,J).NE.1) GO TO 14
       NDS=NDS+1
       DS(NDS)=IJ
       GO TO 11
 14    NDE=NDE+1
       DE=IJ
       GO TO 11
 12    IF (II(IJ,I).NE.1) GO TO 15
       IF (II(IJ,J).NE.2) GO TO 16
```

```
      NSD=NSD+1
      SD(NSD)=IJ
      GO TO 11
 16   IF (II(IJ,J).NE.1) GO TO 17
      NSS=NSS+1
      SS(NSS)=IJ
      GO TO 11
 17   NSE=NSE+1
      SE(NSE)=IJ
      GO TO 11
 15   IF (II(IJ,J).NE.2) GO TO 18
      NED=NED+1
      ED=IJ
      GO TO 11
 18   IF (II(IJ,J).NE.1) GO TO 11
      NES=NES+1
      ES(NES)=IJ
 11   CONTINUE
C  FIGURE OUT NO. OF UNPAIRED ELECTRONS IN ROW AND COLUMN
      NROW=NSD+NSE+NSS
      NCOL=NDS+NES+NSS
C  FIGURE OUT DIFFERENCE IN OCCUPATION
      NDIF=(NSD+NDS+NSE+NES+2*NDE+2*NED)/2
C  FLUSH CONFIGURATIONS WITH MORE THAN 4 UNPAIRED E'S
      IF (NROW.GT.4) GO TO 901
      IF (NCOL.GT.4) GO TO 900
C  FLUSH CONFIGURATIONS DIFFERING IN MORE THAN TWO OCCUPATION
      IF (NDIF.GT.2) GO TO 890
C  START CALCULATING MATRIX ELEMENTS
C  NDIF=0
      IF (NDIF.NE.0) GO TO 100
C   0E/0E
      IF (NROW.NE.0) GO TO 25
C       CODE='000 '
      DO 20 IG=1,N
      IF ((II(IG,I).NE.2).OR.(II(IG,J).NE.2)) GO TO 20
      R(1,1)=R(1,1)+2*HCORE(IG,IG)
      TX(1,1)=TX(1,1)+2*TMX(IG,IG)
      TY(1,1)=TY(1,1)+2*TMY(IG,IG)
 20   CONTINUE
      DO 21 IG=1,N
      DO 21 JG=1,N
      IF ((II(IG,I).NE.2).OR.(II(IG,J).NE.2)) GO TO 21
      IF ((II(JG,I).NE.2).OR.(II(JG,J).NE.2)) GO TO 21
      R(1,1)=R(1,1)+2*GAMMA(IG,IG,JG,JG)-GAMMA (IG,JG,IG,JG)
 21   CONTINUE
      F(IN,JN)=R(1,1)
      TRMX(IN,JN)=TX(1,1)
      TRMY(IN,JN)=TY(1,1)
      GO TO 890
C   2E/2E
 25   IF (NROW.NE.2) GO TO 50
C       CODE='220 '
      DO 40 IG=1,N
      IF ((II(IG,I).NE.2).OR.(II(IG,J).NE.2)) GO TO 40
      R(1,1)=R(1,1)+2*HCORE(IG,IG)
      TX(1,1)=TX(1,1)+2*TMX(IG,IG)
      TY(1,1)=TY(1,1)+2*TMY(IG,IG)
```

```
 40    CONTINUE
       R(1,1)=R(1,1)+HCORE(SS(1),SS(1))+HCORE(SS(2),SS(2))
       TX(1,1)=TX(1,1)+TMX(SS(1),SS(1))+TMX(SS(2),SS(2))
       TY(1,1)=TY(1,1)+TMY(SS(1),SS(1))+TMY(SS(2),SS(2))
       DO 41 IG=1,N
       DO 41 JG=1,N
       IF ((II(IG,I).NE.2).OR.(II(IG,J).NE.2)) GO TO 41
       IF ((II(JG,I).NE.2).OR.(II(JG,J).NE.2)) GO TO 41
       R(1,1)=R(1,1)+2*GAMMA(IG,IG,JG,JG)-GAMMA (IG,JG,IG,JG)
 41    CONTINUE
       DO 42 IG=1,N
       IF ((II(IG,I).NE.2).OR.(II(IG,J).NE.2)) GO TO 42
       R(1,1)=R(1,1)+2*GAMMA(IG,IG,SS(1),SS(1))-GAMMA(IG,SS(1),IG,SS(1))
      *+2*GAMMA(IG,IG,SS(2),SS(2))-GAMMA(IG,SS(2),IG,SS(2))
 42    CONTINUE
       R(1,1)=R(1,1)+GAMMA(SS(1),SS(1),SS(2),SS(2))+GAMMA(SS(1),SS(2),SS(
      *1),SS(2))
       F(IN,JN)=R(1,1)
       TRMX(IN,JN)=TX(1,1)
       TRMY(IN,JN)=TY(1,1)
       GO TO 890
C    4E/4E
 50    IF (NROW.NE.4) GO TO 880
C       CODE='440 '
       DO 70 IG=1,N
       IF ((II(IG,I).NE.2).OR.(II(IG,J).NE.2)) GO TO 70
       R(1,2)=R(1,2)+2*HCORE(IG,IG)
       TX(1,2)=TX(1,2)+2*TMX(IG,IG)
       TY(1,2)=TY(1,2)+2*TMY(IG,IG)
 70    CONTINUE
       R(1,2)=R(1,2)+HCORE(SS(1),SS(1))+HCORE(SS(2),SS(2))+HCORE(SS(3),
      *SS(3))+HCORE(SS(4),SS(4))
       TX(1,2)=TX(1,2)+TMX(SS(1),SS(1))+TMX(SS(2),SS(2))+TMX(SS(3),SS(3))
      *+TMX(SS(4),SS(4))
       TY(1,2)=TY(1,2)+TMY(SS(1),SS(1))+TMY(SS(2),SS(2))+TMY(SS(3),SS(3))
      *+TMY(SS(4),SS(4))
       DO 71 IG=1,N
       DO 71 JG=1,N
       IF ((II(IG,I).NE.2).OR.(II(IG,J).NE.2)) GO TO 71
       IF ((II(JG,I).NE.2).OR.(II(JG,J).NE.2)) GO TO 71
       R(1,2)=R(1,2)+2*GAMMA(IG,IG,JG,JG)-GAMMA(IG,JG,IG,JG)
 71    CONTINUE
       DO 72 IG=1,N
       IF ((II(IG,I).NE.2).OR.(II(IG,J).NE.2)) GO TO 72
       R(1,2)=R(1,2)+2*GAMMA(IG,IG,SS(1),SS(1))-GAMMA(IG,SS(1),IG,SS(1))
      *+2*GAMMA(IG,IG,SS(2),SS(2))-GAMMA(IG,SS(2),IG,SS(2))
      *+2*GAMMA(IG,IG,SS(3),SS(3))-GAMMA(IG,SS(3),IG,SS(3))
      *+2*GAMMA(IG,IG,SS(4),SS(4))-GAMMA(IG,SS(4),IG,SS(4))
 72    CONTINUE
       R(1,2)=R(1,2)+GAMMA(SS(1),SS(1),SS(2),SS(2))
      *+GAMMA(SS(1),SS(1),SS(3),SS(3))+GAMMA(SS(1),SS(1),SS(4),SS(4))
      *+GAMMA(SS(2),SS(2),SS(3),SS(3))+GAMMA(SS(2),SS(2),SS(4),SS(4))
      *+GAMMA(SS(3),SS(3),SS(4),SS(4))
       R(1,1)=R(1,2)-GAMMA(SS(1),SS(2),SS(1),SS(2))-GAMMA(SS(3),SS(4),
      *SS(3),SS(4))
       R(2,2)=R(1,2)-GAMMA(SS(1),SS(3),SS(1),SS(3))-GAMMA(SS(2),SS(4),
      *SS(2),SS(4))
       R(3,3)=R(1,2)-GAMMA(SS(1),SS(4),SS(1),SS(4))-GAMMA(SS(2),SS(3),
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     *SS(2),SS(3))
      R(1,2)=-GAMMA(SS(1),SS(4),SS(1),SS(4))-GAMMA(SS(2),SS(3),SS(2),
     *SS(3))
      R(2,1)=R(1,2)
      R(1,3)=-GAMMA(SS(1),SS(3),SS(1),SS(3))-GAMMA(SS(2),SS(4),SS(2),
     *SS(4))
      R(3,1)=R(1,3)
      R(2,3)=-GAMMA(SS(1),SS(2),SS(1),SS(2))-GAMMA(SS(3),SS(4),SS(3),
     *SS(4))
      R(3,2)=R(2,3)
      TX(1,1)=TX(1,2)
      TX(2,2)=TX(1,2)
      TX(3,3)=TX(1,2)
      TX(1,2)=0.0
      TY(1,1)=TY(1,2)
      TY(2,2)=TY(1,2)
      TY(3,3)=TY(1,2)
      TY(1,2)=0.0
      F(IN,JN)=(4*R(1,1)-2*R(1,2)-2*R(1,3)-2*R(2,1)+R(2,2)+R(2,3)-
     *2*R(3,1)+R(3,2)+R(3,3))/6.0
      F(IN+1,JN+1)=(R(2,2)-R(2,3)-R(3,2)+R(3,3))/2.0
      F(IN,JN+1)=(2*R(1,2)-2*R(1,3)-R(2,2)+R(2,3)-R(3,2)+R(3,3))/
     *SQRT(12.0)
      F(IN+1,JN)=(2*R(2,1)-R(2,2)-R(2,3)-2*R(3,1)+R(3,2)+R(3,3))/
     *SQRT(12.0)
      TRMX(IN,JN)=(4*TX(1,1)+TX(2,2)+TX(3,3))/6.0
      TRMX(IN+1,JN+1)=(TX(2,2)+TX(3,3))/2.0
      TRMY(IN,JN)=(4*TY(1,1)+TY(2,2)+TY(3,3))/6.0
      TRMY(IN+1,JN+1)=(TY(2,2)+TY(3,3))/2.0
      GO TO 890
C  NDIF=1
 100  IF (NDIF.NE.1) GO TO 250
C    0E/2E
      IF (NROW.NE.0) GO TO 2000
C      CODE='021 '
      R(1,1)=HCORE(DS(1),ES(1))
      TX(1,1)=TMX(DS(1),ES(1))
      TY(1,1)=TMY(DS(1),ES(1))
      DO 1990 IG=1,N
      IF ((II(IG,I).NE.2).OR.(II(IG,J).NE.2)) GO TO 1990
      R(1,1)=R(1,1)+2*GAMMA(IG,IG,DS(1),ES(1))-
     *GAMMA(IG,DS(1),IG,ES(1))
 1990 CONTINUE
      R(1,1)=(R(1,1)+GAMMA(DS(1),DS(1),DS(1),ES(1)))*SQRT(2.0)
      TX(1,1)=TX(1,1)*SQRT(2.0)
      TY(1,1)=TY(1,1)*SQRT(2.0)
      GO TO 840
C    2E/0E
 2000 IF (NROW.NE.2) GO TO 175
      IF (NCOL.NE.0) GO TO 2025
C      CODE='201 '
      R(1,1)=HCORE(SD(1),SE(1))
      TX(1,1)=TMX(SD(1),SE(1))
      TY(1,1)=TMY(SD(1),SE(1))
      DO 2010 IG=1,N
      IF ((II(IG,I).NE.2).OR.(II(IG,J).NE.2)) GO TO 2010
      R(1,1)=R(1,1)+2*GAMMA(IG,IG,SD(1),SE(1))-
     *GAMMA(IG,SD(1),IG,SE(1))
```

```
 2010 CONTINUE
      R(1,1)=(R(1,1)+GAMMA(SD(1),SD(1),SD(1),SE(1)))*SQRT(2.0)
      TX(1,1)=TX(1,1)*SQRT(2.0)
      TY(1,1)=TY(1,1)*SQRT(2.0)
      GO TO 840
C   2E/2E
 2025 IF (NCOL.NE.2) GO TO 150
      IF (NSE.NE.1) GO TO 125
C      CODE='221A'
      R(1,1)=HCORE(SE(1),ES(1))
      TX(1,1)=TMX(SE(1),ES(1))
      TY(1,1)=TMY(SE(1),ES(1))
      DO 110 IG=1,N
      IF ((II(IG,I).NE.2).OR.(II(IG,J).NE.2)) GO TO 110
      R(1,1)=R(1,1)+2*GAMMA(IG,IG,SE(1),ES(1))-GAMMA(IG,SE(1),IG,ES(1))
 110  CONTINUE
      R(1,1)=R(1,1)+GAMMA(SS(1),SS(1),SE(1),ES(1))+
     *GAMMA(SS(1),SE(1),SS(1),ES(1))
      GO TO 840
 125  IF (NDS.NE.1) GO TO 880
C      CODE='221B'
      R(1,1)=HCORE(SD(1),DS(1))
      TX(1,1)=TMX(SD(1),DS(1))
      TY(1,1)=TMY(SD(1),DS(1))
      DO 130 IG=1,N
      IF ((II(IG,I).NE.2).OR.(II(IG,J).NE.2)) GO TO 130
      R(1,1)=R(1,1)+2*GAMMA(IG,IG,SD(1),DS(1))-GAMMA(IG,SD(1),IG,DS(1))
 130  CONTINUE
      R(1,1)=R(1,1)+GAMMA(SD(1),SD(1),SD(1),DS(1))+GAMMA(DS(1),DS(1),
     *SD(1),DS(1))+GAMMA(SS(1),SS(1),SD(1),DS(1))-2*GAMMA(SS(1),DS(1),
     *SS(1),SD(1))
      R(1,1)=-R(1,1)
      TX(1,1)=-TX(1,1)
      TY(1,1)=-TY(1,1)
      GO TO 840
C   2E/4E
 150  IF (NDS.NE.1) GO TO 880
C      CODE='241 '
      R(2,2)=HCORE(DS(1),ES(1))
      TX(2,2)=TMX(DS(1),ES(1))
      TY(2,2)=TMY(DS(1),ES(1))
      DO 160 IG=1,N
      IF ((II(IG,I).NE.2).OR.(II(IG,J).NE.2)) GO TO 160
      R(2,2)=R(2,2)+2*GAMMA(IG,IG,DS(1),ES(1))-GAMMA(IG,DS(1),IG,ES(1))
 160  CONTINUE
      R(2,2)=R(2,2)+GAMMA(SS(1),SS(1),DS(1),ES(1))+
     *GAMMA(SS(2),SS(2),DS(1),ES(1))+GAMMA(DS(1),DS(1),DS(1),ES(1))
      R(1,1)=-GAMMA(SS(1),DS(1),SS(1),ES(1))+GAMMA(SS(2),DS(1),SS(2),
     *ES(1))
      R(1,2)=R(2,2)-GAMMA(SS(2),DS(1),SS(2),ES(1))
      R(1,3)=-R(2,2)+GAMMA(SS(1),DS(1),SS(1),ES(1))
      TX(1,2)=TX(2,2)
      TY(1,2)=TY(2,2)
      TX(1,3)=-TX(2,2)
      TY(1,3)=-TY(2,2)
      CALL PERM12S(R,TX,TY,DS,ES,SS,2)
      GO TO 860
C   4E/2E
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 175  IF (NCOL.NE.2) GO TO 200
C      CODE='421 '
      R(2,2)=HCORE(SD(1),SE(1))
      TX(2,2)=TMX(SD(1),SE(1))
      TY(2,2)=TMY(SD(1),SE(1))
      DO 180 IG=1,N
      IF ((II(IG,I).NE.2).OR.(II(IG,J).NE.2)) GO TO 180
      R(2,2)=R(2,2)+2*GAMMA(IG,IG,SD(1),SE(1))-GAMMA(IG,SD(1),IG,SE(1))
 180  CONTINUE
      R(2,2)=R(2,2)+GAMMA(SS(1),SS(1),SD(1),SE(1))+
     *GAMMA(SS(2),SS(2),SD(1),SE(1))+GAMMA(SD(1),SD(1),SD(1),SE(1))
      R(1,1)=-GAMMA(SS(1),SD(1),SS(1),SE(1))+GAMMA(SS(2),SD(1),SS(2),
     *SE(1))
      R(2,1)=R(2,2)-GAMMA(SS(2),SD(1),SS(2),SE(1))
      R(3,1)=-R(2,2)+GAMMA(SS(1),SD(1),SS(1),SE(1))
      TX(2,1)=TX(2,2)
      TY(2,1)=TY(2,2)
      TX(3,1)=-TX(2,2)
      TY(3,1)=-TY(2,2)
      CALL PERM12S(R,TX,TY,SD,SE,SS,1)
      GO TO 870
C   4E/4E
 200  IF (NSE.NE.1) GO TO 225
C      CODE='441A'
      R(1,2)=HCORE(SE(1),ES(1))
      TX(1,2)=TMX(SE(1),ES(1))
      TY(1,2)=TMY(SE(1),ES(1))
      DO 210 IG=1,N
      IF ((II(IG,I).NE.2).OR.(II(IG,J).NE.2)) GO TO 210
      R(1,2)=R(1,2)+2*GAMMA(IG,IG,SE(1),ES(1))-GAMMA(IG,SE(1),IG,ES(1))
 210  CONTINUE
      R(1,2)=R(1,2)+GAMMA(SS(1),SS(1),SE(1),ES(1))+
     *GAMMA(SS(2),SS(2),SE(1),ES(1))+GAMMA(SS(3),SS(3),SE(1),ES(1))
      R(1,1)=R(1,2)-GAMMA(SS(1),SE(1),SS(1),ES(1))
      R(2,2)=R(1,2)-GAMMA(SS(2),SE(1),SS(2),ES(1))
      R(3,3)=R(1,2)-GAMMA(SS(3),SE(1),SS(3),ES(1))
      R(1,2)=-GAMMA(SS(3),SE(1),SS(3),ES(1))
      R(2,1)=R(1,2)
      R(1,3)=-GAMMA(SS(2),SE(1),SS(2),ES(1))
      R(3,1)=R(1,3)
      R(2,3)=-GAMMA(SS(1),SE(1),SS(1),ES(1))
      R(3,2)=R(2,3)
      TX(1,1)=TX(1,2)
      TX(2,2)=TX(1,2)
      TX(3,3)=TX(1,2)
      TX(1,2)=0.0
      TY(1,1)=TY(1,2)
      TY(2,2)=TY(1,2)
      TY(3,3)=TY(1,2)
      TY(1,2)=0.0
      CALL PERM4S(R,TX,TY,SE,SS,1)
      CALL PERM4S(R,TX,TY,ES,SS,2)
      GO TO 850
 225  IF (NDS.NE.1) GO TO 880
C      CODE='441B'
      R(1,2)=HCORE(DS(1),SD(1))
      TX(1,2)=TMX(DS(1),SD(1))
      TY(1,2)=TMY(DS(1),SD(1))
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      DO 230 IG=1,N
      IF ((II(IG,I).NE.2).OR.(II(IG,J).NE.2)) GO TO 230
      R(1,2)=R(1,2)+2*GAMMA(IG,IG,DS(1),SD(1))-GAMMA(IG,DS(1),IG,SD(1))
 230  CONTINUE
      R(1,2)=R(1,2)+GAMMA(DS(1),DS(1),DS(1),SD(1))+
     *GAMMA(SD(1),SD(1),DS(1),SD(1))+GAMMA(SS(1),SS(1),DS(1),SD(1))+
     *GAMMA(SS(2),SS(2),DS(1),SD(1))+GAMMA(SS(3),SS(3),DS(1),SD(1))
      R(1,1)=-R(1,2)+GAMMA(SS(2),DS(1),SS(2),SD(1))+GAMMA(SS(3),DS(1),
     *SS(3),SD(1))
      R(2,2)=-R(1,2)+GAMMA(SS(1),DS(1),SS(1),SD(1))+GAMMA(SS(3),DS(1),
     *SS(3),SD(1))
      R(3,3)=-R(1,2)+GAMMA(SS(1),DS(1),SS(1),SD(1))+GAMMA(SS(2),DS(1),
     *SS(2),SD(1))
      R(1,2)=-GAMMA(SS(3),DS(1),SS(3),SD(1))
      R(2,1)=R(1,2)
      R(1,3)=-GAMMA(SS(2),DS(1),SS(2),SD(1))
      R(3,1)=R(1,3)
      R(2,3)=-GAMMA(SS(1),DS(1),SS(1),SD(1))
      R(3,2)=R(2,3)
      TX(1,1)=-TX(1,2)
      TX(2,2)=-TX(1,2)
      TX(3,3)=-TX(1,2)
      TX(1,2)=0.0
      TY(1,1)=-TY(1,2)
      TY(2,2)=-TY(1,2)
      TY(3,3)=-TY(1,2)
      TY(1,2)=0.0
      CALL PERM4S(R,TX,TY,SD,SS,1)
      CALL PERM4S(R,TX,TY,DS,SS,2)
      GO TO 850
C  NDIF=2
C   0E/0E
 250  IF (NROW.NE.0) GO TO 2125
      IF (NCOL.NE.0) GO TO 2050
C      CODE='002 '
      R(1,1)=GAMMA(DE,ED,DE,ED)
      GO TO 840
C   0E/2E
 2050 IF (NCOL.NE.2) GO TO 2100
      IF (NDE.NE.1) GO TO 2075
C      CODE='022A'
      R(1,1)=GAMMA(DE,ES(1),DE,ES(2))*SQRT(2.0)
      GO TO 840
 2075 IF (NDS.NE.2) GO TO 880
C      CODE='022B'
      R(1,1)=-GAMMA(DS(1),ED,DS(2),ED)*SQRT(2.0)
      GO TO 840
C   0E/4E
 2100 IF (NCOL.NE.4) GO TO 880
C      CODE='042 '
      R(1,2)=-GAMMA(DS(1),ES(2),DS(2),ES(1))*SQRT(2.0)
      R(1,3)=GAMMA(DS(1),ES(1),DS(2),ES(2))*SQRT(2.0)
      R(1,1)=-R(1,2)-R(1,3)
      CALL PERM6S(R,TX,TY,DS,ES,2)
      GO TO 860
C   2E/0E
 2125 IF (NROW.NE.2) GO TO 500
      IF (NCOL.NE.0) GO TO 2175
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      IF (NED.NE.1) GO TO 2150
C      CODE='202A'
      R(1,1)=GAMMA(ED,SE(1),ED,SE(2))*SQRT(2.0)
      GO TO 840
 2150 IF (NSD.NE.2) GO TO 880
C      CODE='202B'
      R(1,1)=-GAMMA(SD(1),DE,SD(2),DE)*SQRT(2.0)
      GO TO 840
C   2E/2E
 2175 IF (NCOL.NE.2) GO TO 400
      IF (NSE.NE.2) GO TO 275
C      CODE='222A'
      R(1,1)=GAMMA(SE(1),ES(1),SE(2),ES(2))+GAMMA(SE(1),ES(2),SE(2),
     *ES(1))
      GO TO 840
 275  IF ((NSE.NE.1).OR.(NSS.NE.0)) GO TO 300
C      CODE='222B'
      R(1,1)=2*GAMMA(DS(1),ES(1),SD(1),SE(1))-GAMMA(DS(1),SD(1),SE(1),
     *ES(1))
      GO TO 840
 300  IF (NSS.NE.2) GO TO 325
C      CODE='222C'
      R(1,1)=GAMMA(DE,ED,DE,ED)
      GO TO 840
 325  IF (NDS.NE.2) GO TO 350
C      CODE='222D'
      R(1,1)=GAMMA(DS(1),SD(1),DS(2),SD(2))+GAMMA(DS(1),SD(2),
     *DS(2),SD(1))
      GO TO 840
 350  IF ((NSE.NE.1).OR.(NSS.NE.1)) GO TO 375
C      CODE='222E'
      R(1,1)=-GAMMA(DS(1),ED,SE(1),ED)
      GO TO 840
 375  IF ((NES.NE.1).OR.(NSS.NE.1)) GO TO 880
C      CODE='222F'
      R(1,1)=-GAMMA(DE,SD(1),DE,ES(1))
      GO TO 840
C   2E/4E
 400  IF (NDS.NE.1) GO TO 425
C      CODE='242A'
      R(1,2)=-GAMMA(DS(1),ES(2),SE(1),ES(1))
      R(1,3)=GAMMA(DS(1),ES(1),SE(1),ES(2))
      R(1,1)=-R(1,2)-R(1,3)
      CALL PERM12S(R,TX,TY,DS,SS,ES,2)
      GO TO 860
 425  IF (NDE.NE.1) GO TO 450
C      CODE='242B'
      R(1,2)=GAMMA(DE,ES(1),DE,ES(2))
      R(1,3)=-R(1,2)
      CALL PERM6S(R,TX,TY,SS,ES,2)
      GO TO 860
 450  IF (NSD.NE.1) GO TO 475
C      CODE='242C'
      R(1,2)=GAMMA(DS(1),ES(1),DS(2),SD(1))
      R(1,3)=-GAMMA(DS(1),SD(1),DS(2),ES(1))
      R(1,1)=-R(1,2)-R(1,3)
      CALL PERM12S(R,TX,TY,SS,ES,DS,2)
      GO TO 860
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 475  IF (NED.NE.1) GO TO 880
C      CODE='242D'
      R(1,2)=-GAMMA(DS(1),ED,DS(2),ED)
      R(1,3)=-R(1,2)
      CALL PERM6S(R,TX,TY,DS,SS,2)
      GO TO 860
C   4E/0E
 500  IF (NCOL.NE.0) GO TO 2200
C      CODE='402 '
      R(2,1)=-GAMMA(SD(1),SE(2),SD(2),SE(1))*SQRT(2.0)
      R(3,1)=GAMMA(SD(1),SE(1),SD(2),SE(2))*SQRT(2.0)
      R(1,1)=-R(2,1)-R(3,1)
      CALL PERM6S(R,TX,TY,SD,SE,1)
      GO TO 870
C   4E/2E
 2200 IF (NCOL.NE.2) GO TO 600
      IF (NSD.NE.1) GO TO 525
C      CODE='422A'
      R(2,1)=-GAMMA(SD(1),SE(2),ES(1),SE(1))
      R(3,1)=GAMMA(SD(1),SE(1),ES(1),SE(2))
      R(1,1)=-R(2,1)-R(3,1)
      CALL PERM12S(R,TX,TY,SD,SS,SE,1)
      GO TO 870
 525  IF (NED.NE.1) GO TO 550
C      CODE='422B'
      R(2,1)=GAMMA(ED,SE(1),ED,SE(2))
      R(3,1)=-R(2,1)
      CALL PERM6S(R,TX,TY,SS,SE,1)
      GO TO 870
 550  IF (NDS.NE.1) GO TO 575
C      CODE='422C'
      R(2,1)=GAMMA(SD(1),SE(1),SD(2),DS(1))
      R(3,1)=-GAMMA(SD(1),DS(1),SD(2),SE(1))
      R(1,1)=-R(2,1)-R(3,1)
      CALL PERM12S(R,TX,TY,SS,SE,SD,1)
      GO TO 870
 575  IF (NDE.NE.1) GO TO 880
C      CODE='422D'
      R(2,1)=-GAMMA(SD(1),DE,SD(2),DE)
      R(3,1)=-R(2,1)
      CALL PERM6S(R,TX,TY,SD,SS,1)
      GO TO 870
C   4E/4E
 600  IF (NSE.NE.2) GO TO 625
C      CODE='442A'
      R(2,2)=GAMMA(SE(1),ES(1),SE(2),ES(2))
      R(3,3)=R(2,2)
      R(2,3)=-GAMMA(SE(1),ES(2),SE(2),ES(1))
      R(3,2)=R(2,3)
      R(1,1)=R(2,2)+R(2,3)
      CALL PERM6S(R,TX,TY,SE,SS,1)
      CALL PERM6S(R,TX,TY,ES,SS,2)
      GO TO 850
 625  IF ((NSE.NE.1).OR.(NSS.NE.2)) GO TO 650
C      CODE='442B'
      R(1,1)=-GAMMA(DS(1),SD(1),SE(1),ES(1))
      R(2,3)=-GAMMA(DS(1),ES(1),SD(1),SE(1))
      R(3,2)=R(2,3)
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      R(2,2)=R(1,1)-R(2,3)
      R(3,3)=R(2,2)
      CALL PERM12S(R,TX,TY,SD,SE,SS,1)
      CALL PERM12S(R,TX,TY,DS,ES,SS,2)
      GO TO 850
 650  IF (NSS.NE.4) GO TO 675
C      CODE='442C'
      R(1,1)=GAMMA(DE,ED,DE,ED)
      R(2,2)=R(1,1)
      R(3,3)=R(1,1)
      GO TO 850
 675  IF (NDS.NE.2) GO TO 700
C      CODE='442D'
      R(2,2)=GAMMA(DS(1),SD(1),DS(2),SD(2))
      R(3,3)=R(2,2)
      R(2,3)=-GAMMA(DS(1),SD(2),DS(2),SD(1))
      R(3,2)=R(2,3)
      R(1,1)=R(2,2)+R(2,3)
      CALL PERM6S(R,TX,TY,SD,SS,1)
      CALL PERM6S(R,TX,TY,DS,SS,2)
      GO TO 850
 700  IF ((NSE.NE.1).OR.(NSS.NE.3)) GO TO 725
C      CODE='442E'
      R(1,1)=-GAMMA(DS(1),ED,SE(1),ED)
      R(2,2)=R(1,1)
      R(3,3)=R(1,1)
      CALL PERM4S(R,TX,TY,SE,SS,1)
      CALL PERM4S(R,TX,TY,DS,SS,2)
      GO TO 850
 725  IF ((NES.NE.1).OR.(NSS.NE.3)) GO TO 880
C      CODE='442F'
      R(1,1)=-GAMMA(SD(1),DE,ES(1),DE)
      R(2,2)=R(1,1)
      R(3,3)=R(1,1)
      CALL PERM4S(R,TX,TY,SD,SS,1)
      CALL PERM4S(R,TX,TY,ES,SS,2)
      GO TO 850
 840  F(IN,JN)=R(1,1)
      F(JN,IN)=R(1,1)
      IF (NDIF.EQ.2) GO TO 890
      TRMX(IN,JN)=TX(1,1)
      TRMX(JN,IN)=TX(1,1)
      TRMY(IN,JN)=TY(1,1)
      TRMY(JN,IN)=TY(1,1)
      GO TO 890
 850  F(IN,JN)=(4*R(1,1)-2*R(1,2)-2*R(1,3)-2*R(2,1)+R(2,2)+R(2,3)-
     *2*R(3,1)+R(3,2)+R(3,3))/6.0
      F(JN,IN)=F(IN,JN)
      F(IN+1,JN+1)=(R(2,2)-R(2,3)-R(3,2)+R(3,3))/2.0
      F(JN+1,IN+1)=F(IN+1,JN+1)
      F(IN,JN+1)=(2*R(1,2)-2*R(1,3)-R(2,2)+R(2,3)-R(3,2)+R(3,3))/
     *SQRT(12.0)
      F(JN+1,IN)=F(IN,JN+1)
      F(IN+1,JN)=(2*R(2,1)-R(2,2)-R(2,3)-2*R(3,1)+R(3,2)+R(3,3))/
     *SQRT(12.0)
      F(JN,IN+1)=F(IN+1,JN)
      IF (NDIF.EQ.2) GO TO 890
      TRMX(IN,JN)=(4*TX(1,1)-2*TX(1,2)-2*TX(1,3)-2*TX(2,1)+
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     *TX(2,2)+TX(2,3)-2*TX(3,1)+TX(3,2)+TX(3,3))/6.0
      TRMX(JN,IN)=TRMX(IN,JN)
      TRMX(IN+1,JN+1)=(TX(2,2)-TX(2,3)-TX(3,2)+TX(3,3))/2.0
      TRMX(JN+1,IN+1)=TRMX(IN+1,JN+1)
      TRMX(IN,JN+1)=(2*TX(1,2)-2*TX(1,3)-TX(2,2)+TX(2,3)-TX(3,2)+
     *TX(3,3))/SQRT(12.0)
      TRMX(JN+1,IN)=TRMX(IN,JN+1)
      TRMX(IN+1,JN)=(2*TX(2,1)-TX(2,2)-TX(2,3)-2*TX(3,1)+TX(3,2)+
     *TX(3,3))/SQRT(12.0)
      TRMX(JN,IN+1)=TRMX(IN+1,JN)
      TRMY(IN,JN)=(4*TY(1,1)-2*TY(1,2)-2*TY(1,3)-2*TY(2,1)+
     *TY(2,2)+TY(2,3)-2*TY(3,1)+TY(3,2)+TY(3,3))/6.0
      TRMY(JN,IN)=TRMY(IN,JN)
      TRMY(IN+1,JN+1)=(TY(2,2)-TY(2,3)-TY(3,2)+TY(3,3))/2.0
      TRMY(JN+1,IN+1)=TRMY(IN+1,JN+1)
      TRMY(IN,JN+1)=(2*TY(1,2)-2*TY(1,3)-TY(2,2)+TY(2,3)-TY(3,2)+
     *TY(3,3))/SQRT(12.0)
      TRMY(JN+1,IN)=TRMY(IN,JN+1)
      TRMY(IN+1,JN)=(2*TY(2,1)-TY(2,2)-TY(2,3)-2*TY(3,1)+TY(3,2)+
     *TY(3,3))/SQRT(12.0)
      TRMY(JN,IN+1)=TRMY(IN+1,JN)
      GO TO 890
  860 F(IN,JN)=(2*R(1,1)-R(1,2)-R(1,3))/SQRT(6.0)
      F(JN,IN)=F(IN,JN)
      F(IN,JN+1)=(R(1,2)-R(1,3))/SQRT(2.0)
      F(JN+1,IN)=F(IN,JN+1)
      IF (NDIF.EQ.2) GO TO 890
      TRMX(IN,JN)=(2*TX(1,1)-TX(1,2)-TX(1,3))/SQRT(6.0)
      TRMX(JN,IN)=TRMX(IN,JN)
      TRMX(IN,JN+1)=(TX(1,2)-TX(1,3))/SQRT(2.0)
      TRMX(JN+1,IN)=TRMX(IN,JN+1)
      TRMY(IN,JN)=(2*TY(1,1)-TY(1,2)-TY(1,3))/SQRT(6.0)
      TRMY(JN,IN)=TRMY(IN,JN)
      TRMY(IN,JN+1)=(TY(1,2)-TY(1,3))/SQRT(2.0)
      TRMY(JN+1,IN)=TRMY(IN,JN+1)
      GO TO 890
  870 F(IN,JN)=(2*R(1,1)-R(2,1)-R(3,1))/SQRT(6.0)
      F(JN,IN)=F(IN,JN)
      F(IN+1,JN)=(R(2,1)-R(3,1))/SQRT(2.0)
      F(JN,IN+1)=F(IN+1,JN)
      IF (NDIF.EQ.2) GO TO 890
      TRMX(IN,JN)=(2*TX(1,1)-TX(2,1)-TX(3,1))/SQRT(6.0)
      TRMX(JN,IN)=TRMX(IN,JN)
      TRMX(IN+1,JN)=(TX(2,1)-TX(3,1))/SQRT(2.0)
      TRMX(JN,IN+1)=TRMX(IN+1,JN)
      TRMY(IN,JN)=(2*TY(1,1)-TY(2,1)-TY(3,1))/SQRT(6.0)
      TRMY(JN,IN)=TRMY(IN,JN)
      TRMY(IN+1,JN)=(TY(2,1)-TY(3,1))/SQRT(2.0)
      TRMY(JN,IN+1)=TRMY(IN+1,JN)
      GO TO 890
  880 WRITE (4,800)
      WRITE (4,801) (II(IJ,I),IJ=1,N)
      WRITE (4,801) (II(IJ,J),IJ=1,N)
C      WRITE (4,802) NDD,NSS,NDS,NSD,NDE,NED,NSE,NES
C      WRITE (4,803) CODE
  800 FORMAT (/' PROBLEM WITH THE FOLLOWING PAIR OF CONFIGURATIONS')
  801 FORMAT (2X,30I2)
C 802  FORMAT (2X,8I3)
```

```
C 803  FORMAT (4X,A4)
 890   CONTINUE
       JN=JN+1
       IF (NCOL.EQ.4) JN=JN+1
 900   CONTINUE
       DO 904 K=1,N
 904   IIN(K,IN)=II(K,I)
       IN=IN+1
       IF (NROW.NE.4) GO TO 901
       DO 905 K=1,N
 905   IIN(K,IN)=II(K,I)
       IN=IN+1
 901   CONTINUE
       IN=IN-1
       MINK=IN
       DO 1000 K=1,MINK
       DO 1000 L=1,N
 1000  II(L,K)=IIN(L,K)
       DO 1001 K=1,MINK
 1001  FDIAG(K)=F(K,K)
C       WRITE (4,1101)
C       DO 1100 I=1,MINK
C       WRITE (4,1102) (F(I,J),J=1,I)
C       WRITE (4,1103)
C 1100 CONTINUE
C       WRITE (4,1201)
C       DO 1200 I=1,MINK
C       WRITE (4,1102) (TRMX(I,J),J=1,I)
C       WRITE (4,1103)
C 1200 CONTINUE
C       WRITE (4,1301)
C       DO 1300 I=1,MINK
C       WRITE (4,1102) (TRMY(I,J),J=1,I)
C       WRITE (4,1103)
C 1300 CONTINUE
C 1101 FORMAT (/' CI MATRIX')
C 1201 FORMAT (/' TRMX MATRIX')
C 1301 FORMAT (/' TRMY MATRIX')
C 1102 FORMAT (10F7.3)
C 1103 FORMAT (/)
       RETURN
       END
C
       SUBROUTINE PERM4S(R,TX,TY,A,B,N)
       DIMENSION R(3,3),TX(3,3),TY(3,3)
       INTEGER A(4),B(4)
       DIMENSION RT(3,3),TXT(3,3),TYT(3,3)
       IF (N.EQ.1) GO TO 10
       DO 5 I=1,3
       DO 5 J=1,3
       RT(I,J)=R(J,I)
       TXT(I,J)=TX(J,I)
 5     TYT(I,J)=TY(J,I)
       GO TO 20
 10    DO 15 I=1,3
       DO 15 J=1,3
       RT(I,J)=R(I,J)
       TXT(I,J)=TX(I,J)
```

```
15    TYT(I,J)=TY(I,J)
20    IF (A(1).LT.B(1)) GO TO 100
      IF (A(1).LT.B(2)) GO TO 90
      IF (A(1).LT.B(3)) GO TO 80
      DO 50 I=1,3
      R(1,I)=RT(1,I)
      RT(1,I)=-RT(3,I)
      RT(2,I)=-RT(2,I)
      RT(3,I)=-R(1,I)
      TX(1,I)=TXT(1,I)
      TXT(1,I)=-TXT(3,I)
      TXT(2,I)=-TXT(2,I)
      TXT(3,I)=-TX(1,I)
      TY(1,I)=TYT(1,I)
      TYT(1,I)=-TYT(3,I)
      TYT(2,I)=-TYT(2,I)
50    TYT(3,I)=-TY(1,I)
      GO TO 100
80    DO 85 I=1,3
      R(1,I)=RT(1,I)
      RT(1,I)=RT(3,I)
      RT(3,I)=RT(2,I)
      RT(2,I)=R(1,I)
      TX(1,I)=TXT(1,I)
      TXT(1,I)=TXT(3,I)
      TXT(3,I)=TXT(2,I)
      TXT(2,I)=TX(1,I)
      TY(1,I)=TYT(1,I)
      TYT(1,I)=TYT(3,I)
      TYT(3,I)=TYT(2,I)
85    TYT(2,I)=TY(1,I)
      GO TO 100
90    DO 95 I=1,3
      RT(1,I)=-RT(1,I)
      R(2,I)=RT(2,I)
      RT(2,I)=-RT(3,I)
      RT(3,I)=-R(2,I)
      TXT(1,I)=-TXT(1,I)
      TX(2,I)=TXT(2,I)
      TXT(2,I)=-TXT(3,I)
      TXT(3,I)=-TX(2,I)
      TYT(1,I)=-TYT(1,I)
      TY(2,I)=TYT(2,I)
      TYT(2,I)=-TYT(3,I)
95    TYT(3,I)=-TY(2,I)
100   IF (N.EQ.1) GO TO 110
      DO 105 I=1,3
      DO 105 J=1,3
      R(I,J)=RT(J,I)
      TX(I,J)=TXT(J,I)
105   TY(I,J)=TYT(J,I)
      GO TO 120
110   DO 115 I=1,3
      DO 115 J=1,3
      R(I,J)=RT(I,J)
      TX(I,J)=TXT(I,J)
115   TY(I,J)=TYT(I,J)
120   RETURN
```

```
      END
C
      SUBROUTINE PERM6S(R,TX,TY,A,B,N)
      DIMENSION R(3,3),TX(3,3),TY(3,3)
      INTEGER A(4),B(4)
      DIMENSION RT(3,3),TXT(3,3),TYT(3,3)
      IF (N.EQ.1) GO TO 10
      DO 5 I=1,3
      DO 5 J=1,3
      RT(I,J)=R(J,I)
      TXT(I,J)=TX(J,I)
 5    TYT(I,J)=TY(J,I)
      GO TO 20
 10   DO 15 I=1,3
      DO 15 J=1,3
      RT(I,J)=R(I,J)
      TXT(I,J)=TX(I,J)
 15   TYT(I,J)=TY(I,J)
 20   IF (A(2).LT.B(1)) GO TO 100
      IF ((A(1).LT.B(1)).AND.(B(1).LT.A(2)).AND.(A(2).LT.B(2))) GO TO 90
      IF ((A(1).LT.B(1)).AND.(B(2).LT.A(2))) GO TO 80
      IF ((B(1).LT.A(1)).AND.(A(2).LT.B(2))) GO TO 80
      IF ((B(1).LT.A(1)).AND.(A(1).LT.B(2)).AND.(B(2).LT.A(2))) GO TO 90
      GO TO 100
 80   DO 85 I=1,3
      R(1,I)=RT(1,I)
      RT(1,I)=RT(2,I)
      RT(2,I)=RT(3,I)
      RT(3,I)=R(1,I)
      TX(1,I)=TXT(1,I)
      TXT(1,I)=TXT(2,I)
      TXT(2,I)=TXT(3,I)
      TXT(3,I)=TX(1,I)
      TY(1,I)=TYT(1,I)
      TYT(1,I)=TYT(2,I)
      TYT(2,I)=TYT(3,I)
 85   TYT(3,I)=TY(1,I)
      GO TO 100
 90   DO 95 I=1,3
      R(1,I)=RT(1,I)
      RT(1,I)=-RT(2,I)
      RT(2,I)=-R(1,I)
      RT(3,I)=-RT(3,I)
      TX(1,I)=TXT(1,I)
      TXT(1,I)=-TXT(2,I)
      TXT(2,I)=-TX(1,I)
      TXT(3,I)=-TXT(3,I)
      TY(1,I)=TYT(1,I)
      TYT(1,I)=-TYT(2,I)
      TYT(2,I)=-TY(1,I)
 95   TYT(3,I)=-TYT(3,I)
 100  IF (N.EQ.1) GO TO 110
      DO 105 I=1,3
      DO 105 J=1,3
      R(I,J)=RT(J,I)
      TX(I,J)=TXT(J,I)
 105  TY(I,J)=TYT(J,I)
      GO TO 120
```

```
 110  DO 115 I=1,3
      DO 115 J=1,3
      R(I,J)=RT(I,J)
      TX(I,J)=TXT(I,J)
 115  TY(I,J)=TYT(I,J)
 120  RETURN
      END
C
      SUBROUTINE PERM12S(R,TX,TY,A,B,C,N)
      DIMENSION R(3,3),TX(3,3),TY(3,3)
      INTEGER A(4),B(4),C(4)
      DIMENSION RT(3,3),TXT(3,3),TYT(3,3)
      IF (N.EQ.1) GO TO 10
      DO 5 I=1,3
      DO 5 J=1,3
      RT(I,J)=R(J,I)
      TXT(I,J)=TX(J,I)
 5    TYT(I,J)=TY(J,I)
      GO TO 20
 10   DO 15 I=1,3
      DO 15 J=1,3
      RT(I,J)=R(I,J)
      TXT(I,J)=TX(I,J)
 15   TYT(I,J)=TY(I,J)
 20   IF ((A(1).LT.B(1)).AND.(B(1).LT.C(1))) GO TO 200
      IF ((B(1).LT.A(1)).AND.(A(1).LT.C(1))) GO TO 190
      IF ((A(1).LT.B(1)).AND.(A(1).GT.C(1)).AND.(B(1).LT.C(2))) GOTO 180
      IF ((B(1).LT.A(1)).AND.(B(1).GT.C(1)).AND.(A(1).LT.C(2))) GOTO 170
      IF ((A(1).LT.B(1)).AND.(A(1).GT.C(2))) GO TO 200
      IF ((B(1).LT.A(1)).AND.(B(1).GT.C(2))) GO TO 190
      IF ((A(1).LT.C(1)).AND.(C(1).LT.B(1)).AND.(B(1).LT.C(2))) GOTO 140
      IF ((B(1).LT.C(1)).AND.(C(1).LT.A(1)).AND.(A(1).LT.C(2))) GOTO 130
      IF ((A(1).LT.C(1)).AND.(C(2).LT.B(1))) GO TO 180
      IF ((B(1).LT.C(1)).AND.(C(2).LT.A(1))) GO TO 170
      IF ((C(1).LT.A(1)).AND.(A(1).LT.C(2)).AND.(C(2).LT.B(1))) GOTO 140
 130  DO 135 I=1,3
      R(1,I)=RT(1,I)
      RT(1,I)=RT(3,I)
      RT(3,I)=RT(2,I)
      RT(2,I)=R(1,I)
      TX(1,I)=TXT(1,I)
      TXT(1,I)=TXT(3,I)
      TXT(3,I)=TXT(2,I)
      TXT(2,I)=TX(1,I)
      TY(1,I)=TYT(1,I)
      TYT(1,I)=TYT(3,I)
      TYT(3,I)=TYT(2,I)
 135  TYT(2,I)=TY(1,I)
      GO TO 200
 140  DO 145 I=1,3
      R(1,I)=RT(1,I)
      RT(1,I)=-RT(2,I)
      RT(2,I)=-R(1,I)
      RT(3,I)=-RT(3,I)
      TX(1,I)=TXT(1,I)
      TXT(1,I)=-TXT(2,I)
      TXT(2,I)=-TX(1,I)
      TXT(3,I)=-TXT(3,I)
```

```
      TY(1,I)=TYT(1,I)
      TYT(1,I)=-TYT(2,I)
      TYT(2,I)=-TY(1,I)
145   TYT(3,I)=-TYT(3,I)
      GO TO 200
170   DO 175 I=1,3
      R(1,I)=RT(1,I)
      RT(1,I)=-RT(3,I)
      RT(2,I)=-RT(2,I)
      RT(3,I)=-R(1,I)
      TX(1,I)=TXT(1,I)
      TXT(1,I)=-TXT(3,I)
      TXT(2,I)=-TXT(2,I)
      TXT(3,I)=-TX(1,I)
      TY(1,I)=TYT(1,I)
      TYT(1,I)=-TYT(3,I)
      TYT(2,I)=-TYT(2,I)
175   TYT(3,I)=-TY(1,I)
      GO TO 200
180   DO 185 I=1,3
      R(1,I)=RT(1,I)
      RT(1,I)=RT(2,I)
      RT(2,I)=RT(3,I)
      RT(3,I)=R(1,I)
      TX(1,I)=TXT(1,I)
      TXT(1,I)=TXT(2,I)
      TXT(2,I)=TXT(3,I)
      TXT(3,I)=TX(1,I)
      TY(1,I)=TYT(1,I)
      TYT(1,I)=TYT(2,I)
      TYT(2,I)=TYT(3,I)
185   TYT(3,I)=TY(1,I)
      GO TO 200
190   DO 195 I=1,3
      RT(1,I)=-RT(1,I)
      R(2,I)=RT(2,I)
      RT(2,I)=-RT(3,I)
      RT(3,I)=-R(2,I)
      TXT(1,I)=-TXT(1,I)
      TX(2,I)=TXT(2,I)
      TXT(2,I)=-TXT(3,I)
      TXT(3,I)=-TX(2,I)
      TYT(1,I)=-TYT(1,I)
      TY(2,I)=TYT(2,I)
      TYT(2,I)=-TYT(3,I)
195   TYT(3,I)=-TY(2,I)
200   IF (N.EQ.1) GO TO 210
      DO 205 I=1,3
      DO 205 J=1,3
      R(I,J)=RT(J,I)
      TX(I,J)=TXT(J,I)
205   TY(I,J)=TYT(J,I)
      GO TO 220
210   DO 215 I=1,3
      DO 215 J=1,3
      R(I,J)=RT(I,J)
      TX(I,J)=TXT(I,J)
215   TY(I,J)=TYT(I,J)
```

```
 220  RETURN
      END
C
      SUBROUTINE CIEXI3(MINK,F,FDIAG,II,TRMX,TRMY)
      COMMON N,H,G,X,Y,C
      DIMENSION H(30,30),G(30,30),C(30,30),X(30),Y(30)
      DIMENSION II(30,500),F(500,500),FDIAG(500),TRMX(500,500)
      DIMENSION TRMY(500,500),IIN(30,500)
      DIMENSION R(3,3),TX(3,3),TY(3,3)
      INTEGER SS(4),DS(4),SD(4),SE(4),ES(4),DE,ED
C      INTEGER DD(15)
C      CHARACTER*4 CODE
      MNK=3*MINK
      DO 1950 I=1,MNK
      DO 1950 J=1,MNK
      F(I,J)=0.0
      TRMY(I,J)=0.0
 1950 TRMX(I,J)=0.0
      IN=1
      DO 901 I=1,MINK
      JN=1
      DO 900 J=1,I
      DO 10 K=1,3
      DO 10 L=1,3
      R(K,L)=0.0
      TX(K,L)=0.0
 10   TY(K,L)=0.0
C      NDD=0
      NSS=0
      NDS=0
      NSD=0
      NSE=0
      NES=0
      NDE=0
      NED=0
C  IDENTIFY OCCUPATION PATTERNS
      DO 11 IJ=1,N
      IF (II(IJ,I).NE.2) GO TO 12
      IF (II(IJ,J).NE.2) GO TO 13
C      NDD=NDD+1
C      DD(NDD)=IJ
      GO TO 11
 13   IF (II(IJ,J).NE.1) GO TO 14
      NDS=NDS+1
      DS(NDS)=IJ
      GO TO 11
 14   NDE=NDE+1
      DE=IJ
      GO TO 11
 12   IF (II(IJ,I).NE.1) GO TO 15
      IF (II(IJ,J).NE.2) GO TO 16
      NSD=NSD+1
      SD(NSD)=IJ
      GO TO 11
 16   IF (II(IJ,J).NE.1) GO TO 17
      NSS=NSS+1
      SS(NSS)=IJ
      GO TO 11
```

```
 17   NSE=NSE+1
      SE(NSE)=IJ
      GO TO 11
 15   IF (II(IJ,J).NE.2) GO TO 18
      NED=NED+1
      ED=IJ
      GO TO 11
 18   IF (II(IJ,J).NE.1) GO TO 11
      NES=NES+1
      ES(NES)=IJ
 11   CONTINUE
C  FIGURE OUT NO. OF UNPAIRED ELECTRONS IN ROW AND COLUMN
      NROW=NSD+NSE+NSS
      NCOL=NDS+NES+NSS
C  FIGURE OUT DIFFERENCE IN OCCUPATION
      NDIF=(NSD+NDS+NSE+NES+2*NDE+2*NED)/2
C  FLUSH CONFIGURATIONS WITH CLOSED SHELL OR GT. 4 UNPAIRED E'S
      IF ((NROW.EQ.0).OR.(NROW.GT.4)) GO TO 901
      IF ((NCOL.EQ.0).OR.(NCOL.GT.4)) GO TO 900
C  FLUSH CONFIGURATIONS DIFFERING IN MORE THAN TWO OCCUPATION
      IF (NDIF.GT.2) GO TO 890
C  START CALCULATING MATRIX ELEMENTS
C  NDIF=0
      IF (NDIF.NE.0) GO TO 100
C   2E/2E
      IF (NROW.NE.2) GO TO 50
C       CODE='220 '
      DO 20 IG=1,N
      IF ((II(IG,I).NE.2).OR.(II(IG,J).NE.2)) GO TO 20
      R(1,1)=R(1,1)+2*HCORE(IG,IG)
      TX(1,1)=TX(1,1)+2*TMX(IG,IG)
      TY(1,1)=TY(1,1)+2*TMY(IG,IG)
 20   CONTINUE
      R(1,1)=R(1,1)+HCORE(SS(1),SS(1))+HCORE(SS(2),SS(2))
      TX(1,1)=TX(1,1)+TMX(SS(1),SS(1))+TMX(SS(2),SS(2))
      TY(1,1)=TY(1,1)+TMY(SS(1),SS(1))+TMY(SS(2),SS(2))
      DO 21 IG=1,N
      DO 21 JG=1,N
      IF ((II(IG,I).NE.2).OR.(II(IG,J).NE.2)) GO TO 21
      IF ((II(JG,I).NE.2).OR.(II(JG,J).NE.2)) GO TO 21
      R(1,1)=R(1,1)+2*GAMMA(IG,IG,JG,JG)-GAMMA (IG,JG,IG,JG)
 21   CONTINUE
      DO 22 IG=1,N
      IF ((II(IG,I).NE.2).OR.(II(IG,J).NE.2)) GO TO 22
      R(1,1)=R(1,1)+2*GAMMA(IG,IG,SS(1),SS(1))-GAMMA(IG,SS(1),IG,SS(1))
     *+2*GAMMA(IG,IG,SS(2),SS(2))-GAMMA(IG,SS(2),IG,SS(2))
 22   CONTINUE
      R(1,1)=R(1,1)+GAMMA(SS(1),SS(1),SS(2),SS(2))-GAMMA(SS(1),SS(2),SS(
     *1),SS(2))
      F(IN,JN)=R(1,1)
      TRMX(IN,JN)=TX(1,1)
      TRMY(IN,JN)=TY(1,1)
      GO TO 890
C   4E/4E
 50   IF (NROW.NE.4) GO TO 880
C       CODE='440 '
      DO 70 IG=1,N
      IF ((II(IG,I).NE.2).OR.(II(IG,J).NE.2)) GO TO 70
```

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      R(1,2)=R(1,2)+2*HCORE(IG,IG)
      TX(1,2)=TX(1,2)+2*TMX(IG,IG)
      TY(1,2)=TY(1,2)+2*TMY(IG,IG)
 70   CONTINUE
      R(1,2)=R(1,2)+HCORE(SS(1),SS(1))+HCORE(SS(2),SS(2))+HCORE(SS(3),
     *SS(3))+HCORE(SS(4),SS(4))
      TX(1,2)=TX(1,2)+TMX(SS(1),SS(1))+TMX(SS(2),SS(2))+TMX(SS(3),SS(3))
     *+TMX(SS(4),SS(4))
      TY(1,2)=TY(1,2)+TMY(SS(1),SS(1))+TMY(SS(2),SS(2))+TMY(SS(3),SS(3))
     *+TMY(SS(4),SS(4))
      DO 71 IG=1,N
      DO 71 JG=1,N
      IF ((II(IG,I).NE.2).OR.(II(IG,J).NE.2)) GO TO 71
      IF ((II(JG,I).NE.2).OR.(II(JG,J).NE.2)) GO TO 71
      R(1,2)=R(1,2)+2*GAMMA(IG,IG,JG,JG)-GAMMA(IG,JG,IG,JG)
 71   CONTINUE
      DO 72 IG=1,N
      IF ((II(IG,I).NE.2).OR.(II(IG,J).NE.2)) GO TO 72
      R(1,2)=R(1,2)+2*GAMMA(IG,IG,SS(1),SS(1))-GAMMA(IG,SS(1),IG,SS(1))
     *+2*GAMMA(IG,IG,SS(2),SS(2))-GAMMA(IG,SS(2),IG,SS(2))
     *+2*GAMMA(IG,IG,SS(3),SS(3))-GAMMA(IG,SS(3),IG,SS(3))
     *+2*GAMMA(IG,IG,SS(4),SS(4))-GAMMA(IG,SS(4),IG,SS(4))
 72   CONTINUE
      R(1,2)=R(1,2)+GAMMA(SS(1),SS(1),SS(2),SS(2))
     *+GAMMA(SS(1),SS(1),SS(3),SS(3))+GAMMA(SS(1),SS(1),SS(4),SS(4))
     *+GAMMA(SS(2),SS(2),SS(3),SS(3))+GAMMA(SS(2),SS(2),SS(4),SS(4))
     *+GAMMA(SS(3),SS(3),SS(4),SS(4))
      F(IN,JN)=R(1,2)-GAMMA(SS(1),SS(2),SS(1),SS(2))-
     *GAMMA(SS(3),SS(4),SS(3),SS(4))
      F(IN+1,JN+1)=R(1,2)-GAMMA(SS(1),SS(3),SS(1),SS(3))-
     *GAMMA(SS(2),SS(4),SS(2),SS(4))
      F(IN+2,JN+2)=R(1,2)-GAMMA(SS(1),SS(4),SS(1),SS(4))-
     *GAMMA(SS(2),SS(3),SS(2),SS(3))
      F(IN,JN+1)=GAMMA(SS(1),SS(4),SS(1),SS(4))-
     *GAMMA(SS(2),SS(3),SS(2),SS(3))
      F(JN+1,IN)=F(IN,JN+1)
      F(IN,JN+2)=GAMMA(SS(1),SS(3),SS(1),SS(3))-
     *GAMMA(SS(2),SS(4),SS(2),SS(4))
      F(JN+2,IN)=F(IN,JN+2)
      F(IN+1,JN+2)=GAMMA(SS(1),SS(2),SS(1),SS(2))-
     *GAMMA(SS(3),SS(4),SS(3),SS(4))
      F(JN+2,IN+1)=F(IN+1,JN+2)
      TRMX(IN,JN)=TX(1,2)
      TRMX(IN+1,JN+1)=TX(1,2)
      TRMX(IN+2,JN+2)=TX(1,2)
      TRMY(IN,JN)=TY(1,2)
      TRMY(IN+1,JN+1)=TY(1,2)
      TRMY(IN+2,JN+2)=TY(1,2)
      GO TO 890
C  NDIF=1
 100  IF (NDIF.NE.1) GO TO 250
C    2E/2E
      IF (NROW.NE.2) GO TO 175
      IF (NCOL.NE.2) GO TO 150
      IF (NSE.NE.1) GO TO 125
C      CODE='221A'
      R(1,1)=HCORE(SE(1),ES(1))
      TX(1,1)=TMX(SE(1),ES(1))
```

```
      TY(1,1)=TMY(SE(1),ES(1))
      DO 110 IG=1,N
      IF ((II(IG,I).NE.2).OR.(II(IG,J).NE.2)) GO TO 110
      R(1,1)=R(1,1)+2*GAMMA(IG,IG,SE(1),ES(1))-GAMMA(IG,SE(1),IG,ES(1))
 110  CONTINUE
      R(1,1)=R(1,1)+GAMMA(SS(1),SS(1),SE(1),ES(1))-
     *GAMMA(SS(1),SE(1),SS(1),ES(1))
      CALL PERM2T(R,TX,TY,SE,SS,1)
      CALL PERM2T(R,TX,TY,ES,SS,2)
      GO TO 840
 125  IF (NDS.NE.1) GO TO 880
C      CODE='221B'
      R(1,1)=HCORE(SD(1),DS(1))
      TX(1,1)=TMX(SD(1),DS(1))
      TY(1,1)=TMY(SD(1),DS(1))
      DO 130 IG=1,N
      IF ((II(IG,I).NE.2).OR.(II(IG,J).NE.2)) GO TO 130
      R(1,1)=R(1,1)+2*GAMMA(IG,IG,SD(1),DS(1))-GAMMA(IG,SD(1),IG,DS(1))
 130  CONTINUE
      R(1,1)=R(1,1)+GAMMA(SD(1),SD(1),SD(1),DS(1))+GAMMA(DS(1),DS(1),
     *SD(1),DS(1))+GAMMA(SS(1),SS(1),SD(1),DS(1))
      R(1,1)=-R(1,1)
      TX(1,1)=-TX(1,1)
      TY(1,1)=-TY(1,1)
      CALL PERM2T(R,TX,TY,SD,SS,1)
      CALL PERM2T(R,TX,TY,DS,SS,2)
      GO TO 840
C   2E/4E
 150  IF (NDS.NE.1) GO TO 880
C      CODE='241 '
      R(2,2)=HCORE(DS(1),ES(1))
      TX(2,2)=TMX(DS(1),ES(1))
      TY(2,2)=TMY(DS(1),ES(1))
      DO 160 IG=1,N
      IF ((II(IG,I).NE.2).OR.(II(IG,J).NE.2)) GO TO 160
      R(2,2)=R(2,2)+2*GAMMA(IG,IG,DS(1),ES(1))-GAMMA(IG,DS(1),IG,ES(1))
 160  CONTINUE
      R(2,2)=R(2,2)+GAMMA(SS(1),SS(1),DS(1),ES(1))+
     *GAMMA(SS(2),SS(2),DS(1),ES(1))+GAMMA(DS(1),DS(1),DS(1),ES(1))
      R(1,1)=-GAMMA(SS(1),DS(1),SS(1),ES(1))-GAMMA(SS(2),DS(1),SS(2),
     *ES(1))
      R(1,2)=R(2,2)-GAMMA(SS(2),DS(1),SS(2),ES(1))
      R(1,3)=R(2,2)-GAMMA(SS(1),DS(1),SS(1),ES(1))
      TX(1,2)=TX(2,2)
      TY(1,2)=TY(2,2)
      TX(1,3)=TX(2,2)
      TY(1,3)=TY(2,2)
      CALL PERM12T(R,TX,TY,DS,ES,SS,2)
      GO TO 860
C   4E/2E
 175  IF (NCOL.NE.2) GO TO 200
C      CODE='421 '
      R(2,2)=HCORE(SD(1),SE(1))
      TX(2,2)=TMX(SD(1),SE(1))
      TY(2,2)=TMY(SD(1),SE(1))
      DO 180 IG=1,N
      IF ((II(IG,I).NE.2).OR.(II(IG,J).NE.2)) GO TO 180
      R(2,2)=R(2,2)+2*GAMMA(IG,IG,SD(1),SE(1))-GAMMA(IG,SD(1),IG,SE(1))
```

```
 180  CONTINUE
      R(2,2)=R(2,2)+GAMMA(SS(1),SS(1),SD(1),SE(1))+
     *GAMMA(SS(2),SS(2),SD(1),SE(1))+GAMMA(SD(1),SD(1),SD(1),SE(1))
      R(1,1)=-GAMMA(SS(1),SD(1),SS(1),SE(1))-GAMMA(SS(2),SD(1),SS(2),
     *SE(1))
      R(2,1)=R(2,2)-GAMMA(SS(2),SD(1),SS(2),SE(1))
      R(3,1)=R(2,2)-GAMMA(SS(1),SD(1),SS(1),SE(1))
      TX(2,1)=TX(2,2)
      TY(2,1)=TY(2,2)
      TX(3,1)=TX(2,2)
      TY(3,1)=TY(2,2)
      CALL PERM12T(R,TX,TY,SD,SE,SS,1)
      GO TO 870
C   4E/4E
 200  IF (NSE.NE.1) GO TO 225
C      CODE='441A'
      R(1,2)=HCORE(SE(1),ES(1))
      TX(1,2)=TMX(SE(1),ES(1))
      TY(1,2)=TMY(SE(1),ES(1))
      DO 210 IG=1,N
      IF ((II(IG,I).NE.2).OR.(II(IG,J).NE.2)) GO TO 210
      R(1,2)=R(1,2)+2*GAMMA(IG,IG,SE(1),ES(1))-GAMMA(IG,SE(1),IG,ES(1))
 210  CONTINUE
      R(1,2)=R(1,2)+GAMMA(SS(1),SS(1),SE(1),ES(1))+
     *GAMMA(SS(2),SS(2),SE(1),ES(1))+GAMMA(SS(3),SS(3),SE(1),ES(1))
      R(1,1)=R(1,2)-GAMMA(SS(1),SE(1),SS(1),ES(1))
      R(2,2)=R(1,2)-GAMMA(SS(2),SE(1),SS(2),ES(1))
      R(3,3)=R(1,2)-GAMMA(SS(3),SE(1),SS(3),ES(1))
      R(1,2)=GAMMA(SS(3),SE(1),SS(3),ES(1))
      R(2,1)=R(1,2)
      R(1,3)=GAMMA(SS(2),SE(1),SS(2),ES(1))
      R(3,1)=R(1,3)
      R(2,3)=GAMMA(SS(1),SE(1),SS(1),ES(1))
      R(3,2)=R(2,3)
      TX(1,1)=TX(1,2)
      TX(2,2)=TX(1,2)
      TX(3,3)=TX(1,2)
      TX(1,2)=0.0
      TY(1,1)=TY(1,2)
      TY(2,2)=TY(1,2)
      TY(3,3)=TY(1,2)
      TY(1,2)=0.0
      CALL PERM4T(R,TX,TY,SE,SS,1)
      CALL PERM4T(R,TX,TY,ES,SS,2)
      GO TO 850
 225  IF (NDS.NE.1) GO TO 880
C      CODE='441B'
      R(1,2)=HCORE(DS(1),SD(1))
      TX(1,2)=TMX(DS(1),SD(1))
      TY(1,2)=TMY(DS(1),SD(1))
      DO 230 IG=1,N
      IF ((II(IG,I).NE.2).OR.(II(IG,J).NE.2)) GO TO 230
      R(1,2)=R(1,2)+2*GAMMA(IG,IG,DS(1),SD(1))-GAMMA(IG,DS(1),IG,SD(1))
 230  CONTINUE
      R(1,2)=R(1,2)+GAMMA(DS(1),DS(1),DS(1),SD(1))+
     *GAMMA(SD(1),SD(1),DS(1),SD(1))+GAMMA(SS(1),SS(1),DS(1),SD(1))+
     *GAMMA(SS(2),SS(2),DS(1),SD(1))+GAMMA(SS(3),SS(3),DS(1),SD(1))
      R(1,1)=-R(1,2)+GAMMA(SS(2),DS(1),SS(2),SD(1))+GAMMA(SS(3),DS(1),
```

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     *SS(3),SD(1))
      R(2,2)=-R(1,2)+GAMMA(SS(1),DS(1),SS(1),SD(1))+GAMMA(SS(3),DS(1),
     *SS(3),SD(1))
      R(3,3)=-R(1,2)+GAMMA(SS(1),DS(1),SS(1),SD(1))+GAMMA(SS(2),DS(1),
     *SS(2),SD(1))
      R(1,2)=GAMMA(SS(3),DS(1),SS(3),SD(1))
      R(2,1)=R(1,2)
      R(1,3)=GAMMA(SS(2),DS(1),SS(2),SD(1))
      R(3,1)=R(1,3)
      R(2,3)=GAMMA(SS(1),DS(1),SS(1),SD(1))
      R(3,2)=R(2,3)
      TX(1,1)=-TX(1,2)
      TX(2,2)=-TX(1,2)
      TX(3,3)=-TX(1,2)
      TX(1,2)=0.0
      TY(1,1)=-TY(1,2)
      TY(2,2)=-TY(1,2)
      TY(3,3)=-TY(1,2)
      TY(1,2)=0.0
      CALL PERM4T(R,TX,TY,SD,SS,1)
      CALL PERM4T(R,TX,TY,DS,SS,2)
      GO TO 850
C  NDIF=2
C   2E/2E
 250  IF (NROW.NE.2) GO TO 500
      IF (NCOL.NE.2) GO TO 400
      IF (NSE.NE.2) GO TO 275
C      CODE='222A'
      R(1,1)=GAMMA(SE(1),ES(1),SE(2),ES(2))-GAMMA(SE(1),ES(2),SE(2),
     *ES(1))
      GO TO 840
 275  IF ((NSE.NE.1).OR.(NSS.NE.0)) GO TO 300
C      CODE='222B'
      R(1,1)=-GAMMA(DS(1),SD(1),SE(1),ES(1))
      CALL PERM2T(R,TX,TY,SD,SE,1)
      CALL PERM2T(R,TX,TY,DS,ES,2)
      GO TO 840
 300  IF (NSS.NE.2) GO TO 325
C      CODE='222C'
      R(1,1)=GAMMA(DE,ED,DE,ED)
      GO TO 840
 325  IF (NDS.NE.2) GO TO 350
C      CODE='222D'
      R(1,1)=GAMMA(DS(1),SD(1),DS(2),SD(2))-GAMMA(DS(1),SD(2),
     *DS(2),SD(1))
      GO TO 840
 350  IF ((NSE.NE.1).OR.(NSS.NE.1)) GO TO 375
C      CODE='222E'
      R(1,1)=GAMMA(DS(1),ED,SE(1),ED)
      CALL PERM2T(R,TX,TY,SS,SE,1)
      CALL PERM2T(R,TX,TY,DS,SS,2)
      GO TO 840
 375  IF ((NES.NE.1).OR.(NSS.NE.1)) GO TO 880
C      CODE='222F'
      R(1,1)=GAMMA(DE,SD(1),DE,ES(1))
      CALL PERM2T(R,TX,TY,SD,SS,1)
      CALL PERM2T(R,TX,TY,SS,ES,2)
      GO TO 840
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C   2E/4E
 400  IF (NDS.NE.1) GO TO 425
C      CODE='242A'
      R(1,2)=GAMMA(DS(1),ES(2),SE(1),ES(1))
      R(1,3)=-GAMMA(DS(1),ES(1),SE(1),ES(2))
      R(1,1)=R(1,2)+R(1,3)
      CALL PERM2T(R,TX,TY,SS,SE,1)
      CALL PERM12T(R,TX,TY,DS,SS,ES,2)
      GO TO 860
 425  IF (NDE.NE.1) GO TO 450
C      CODE='242B'
      R(1,2)=GAMMA(DE,ES(1),DE,ES(2))
      R(1,3)=-R(1,2)
      CALL PERM6T(R,TX,TY,SS,ES,2)
      GO TO 860
 450  IF (NSD.NE.1) GO TO 475
C      CODE='242C'
      R(1,2)=-GAMMA(DS(1),ES(1),DS(2),SD(1))
      R(1,3)=GAMMA(DS(1),SD(1),DS(2),ES(1))
      R(1,1)=-R(1,2)-R(1,3)
      CALL PERM2T(R,TX,TY,SD,SS,1)
      CALL PERM12T(R,TX,TY,SS,ES,DS,2)
      GO TO 860
 475  IF (NED.NE.1) GO TO 880
C      CODE='242D'
      R(1,2)=-GAMMA(DS(1),ED,DS(2),ED)
      R(1,3)=R(1,2)
      CALL PERM6T(R,TX,TY,DS,SS,2)
      GO TO 860
C   4E/2E
 500  IF (NCOL.NE.2) GO TO 600
      IF (NSD.NE.1) GO TO 525
C      CODE='422A'
      R(2,1)=GAMMA(SD(1),SE(2),ES(1),SE(1))
      R(3,1)=-GAMMA(SD(1),SE(1),ES(1),SE(2))
      R(1,1)=R(2,1)+R(3,1)
      CALL PERM2T(R,TX,TY,SS,ES,2)
      CALL PERM12T(R,TX,TY,SD,SS,SE,1)
      GO TO 870
 525  IF (NED.NE.1) GO TO 550
C      CODE='422B'
      R(2,1)=GAMMA(ED,SE(1),ED,SE(2))
      R(3,1)=-R(2,1)
      CALL PERM6T(R,TX,TY,SS,SE,1)
      GO TO 870
 550  IF (NDS.NE.1) GO TO 575
C      CODE='422C'
      R(2,1)=-GAMMA(SD(1),SE(1),SD(2),DS(1))
      R(3,1)=GAMMA(SD(1),DS(1),SD(2),SE(1))
      R(1,1)=-R(2,1)-R(3,1)
      CALL PERM2T(R,TX,TY,DS,SS,2)
      CALL PERM12T(R,TX,TY,SS,SE,SD,1)
      GO TO 870
 575  IF (NDE.NE.1) GO TO 880
C      CODE='422D'
      R(2,1)=-GAMMA(SD(1),DE,SD(2),DE)
      R(3,1)=R(2,1)
      CALL PERM6T(R,TX,TY,SD,SS,1)
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      GO TO 870
C   4E/4E
  600 IF (NSE.NE.2) GO TO 625
C      CODE='442A'
      R(2,2)=GAMMA(SE(1),ES(1),SE(2),ES(2))
      R(3,3)=R(2,2)
      R(2,3)=GAMMA(SE(1),ES(2),SE(2),ES(1))
      R(3,2)=R(2,3)
      R(1,1)=R(2,2)-R(2,3)
      CALL PERM6T(R,TX,TY,SE,SS,1)
      CALL PERM6T(R,TX,TY,ES,SS,2)
      GO TO 850
  625 IF ((NSE.NE.1).OR.(NSS.NE.2)) GO TO 650
C      CODE='442B'
      R(1,1)=-GAMMA(DS(1),SD(1),SE(1),ES(1))
      R(2,3)=GAMMA(DS(1),ES(1),SD(1),SE(1))
      R(3,2)=R(2,3)
      R(2,2)=R(1,1)+R(2,3)
      R(3,3)=R(2,2)
      CALL PERM12T(R,TX,TY,SD,SE,SS,1)
      CALL PERM12T(R,TX,TY,DS,ES,SS,2)
      GO TO 850
  650 IF (NSS.NE.4) GO TO 675
C      CODE='442C'
      R(1,1)=GAMMA(DE,ED,DE,ED)
      R(2,2)=R(1,1)
      R(3,3)=R(1,1)
      GO TO 850
  675 IF (NDS.NE.2) GO TO 700
      CODE='442D'
      R(2,2)=GAMMA(DS(1),SD(1),DS(2),SD(2))
      R(3,3)=R(2,2)
      R(2,3)=GAMMA(DS(1),SD(2),DS(2),SD(1))
      R(3,2)=R(2,3)
      R(1,1)=R(2,2)-R(2,3)
      CALL PERM6T(R,TX,TY,SD,SS,1)
      CALL PERM6T(R,TX,TY,DS,SS,2)
      GO TO 850
  700 IF ((NSE.NE.1).OR.(NSS.NE.3)) GO TO 725
      CODE='442E'
      R(1,1)=-GAMMA(DS(1),ED,SE(1),ED)
      R(2,2)=R(1,1)
      R(3,3)=R(1,1)
      CALL PERM4T(R,TX,TY,SE,SS,1)
      CALL PERM4T(R,TX,TY,DS,SS,2)
      GO TO 850
  725 IF ((NES.NE.1).OR.(NSS.NE.3)) GO TO 880
      CODE='442F'
      R(1,1)=-GAMMA(SD(1),DE,ES(1),DE)
      R(2,2)=R(1,1)
      R(3,3)=R(1,1)
      CALL PERM4T(R,TX,TY,SD,SS,1)
      CALL PERM4T(R,TX,TY,ES,SS,2)
      GO TO 850
  840 F(IN,JN)=R(1,1)
      F(JN,IN)=R(1,1)
      IF (NDIF.EQ.2) GO TO 890
      TRMX(IN,JN)=TX(1,1)
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      TRMX(JN,IN)=TX(1,1)
      TRMY(IN,JN)=TY(1,1)
      TRMY(JN,IN)=TY(1,1)
      GO TO 890
  850 DO 851 KK=1,3
      DO 851 LL=1,3
      F(IN+KK-1,JN+LL-1)=R(KK,LL)
      F(JN+LL-1,IN+KK-1)=R(KK,LL)
      IF (NDIF.EQ.2) GO TO 851
      TRMX(IN+KK-1,JN+LL-1)=TX(KK,LL)
      TRMX(JN+LL-1,IN+KK-1)=TX(KK,LL)
      TRMY(IN+KK-1,JN+LL-1)=TY(KK,LL)
      TRMY(JN+LL-1,IN+KK-1)=TY(KK,LL)
  851 CONTINUE
      GO TO 890
  860 DO 861 KK=1,3
      F(IN,JN+KK-1)=R(1,KK)
      F(JN+KK-1,IN)=R(1,KK)
      IF (NDIF.EQ.2) GO TO 861
      TRMX(IN,JN+KK-1)=TX(1,KK)
      TRMX(JN+KK-1,IN)=TX(1,KK)
      TRMY(IN,JN+KK-1)=TY(1,KK)
      TRMY(JN+KK-1,IN)=TY(1,KK)
  861 CONTINUE
      GO TO 890
  870 DO 871 KK=1,3
      F(IN+KK-1,JN)=R(KK,1)
      F(JN,IN+KK-1)=R(KK,1)
      IF (NDIF.EQ.2) GO TO 871
      TRMX(IN+KK-1,JN)=TX(KK,1)
      TRMX(JN,IN+KK-1)=TX(KK,1)
      TRMY(IN+KK-1,JN)=TY(KK,1)
      TRMY(JN,IN+KK-1)=TY(KK,1)
  871 CONTINUE
      GO TO 890
  880 WRITE (4,800)
      WRITE (4,801) (II(IJ,I),IJ=1,N)
      WRITE (4,801) (II(IJ,J),IJ=1,N)
C      WRITE (4,802) NDD,NSS,NDS,NSD,NDE,NED,NSE,NES
C      WRITE (4,803) CODE
  800 FORMAT (/' PROBLEM WITH THE FOLLOWING PAIR OF CONFIGURATIONS')
  801 FORMAT (2X,30I2)
C 802 FORMAT (2X,8I3)
C 803 FORMAT (4X,A4)
  890 CONTINUE
      JN=JN+1
      IF (NCOL.EQ.4) JN=JN+2
  900 CONTINUE
      DO 904 K=1,N
  904 IIN(K,IN)=II(K,I)
      IN=IN+1
      IF (NROW.NE.4) GO TO 901
      DO 905 K=1,N
      IIN(K,IN)=II(K,I)
  905 IIN(K,IN+1)=II(K,I)
      IN=IN+2
  901 CONTINUE
      IN=IN-1
```

```
      MINK=IN
      DO 1000 K=1,MINK
      DO 1000 L=1,N
 1000 II(L,K)=IIN(L,K)
      DO 1001 K=1,MINK
 1001 FDIAG(K)=F(K,K)
C      WRITE (4,1101)
C      DO 1100 I=1,MINK
C      WRITE (4,1102) (F(I,J),J=1,I)
C      WRITE (4,1103)
C 1100 CONTINUE
C      WRITE (4,1201)
C      DO 1200 I=1,MINK
C      WRITE (4,1102) (TRMX(I,J),J=1,I)
C      WRITE (4,1103)
C 1200 CONTINUE
C      WRITE (4,1301)
C      DO 1300 I=1,MINK
C      WRITE (4,1102) (TRMY(I,J),J=1,I)
C      WRITE (4,1103)
C 1300 CONTINUE
C 1101 FORMAT (/' CI MATRIX')
C 1201 FORMAT (/' TRMX MATRIX')
C 1301 FORMAT (/' TRMY MATRIX')
C 1102 FORMAT (10F7.3)
C 1103 FORMAT (/)
      RETURN
      END
C
      SUBROUTINE PERM2T(R,TX,TY,A,B,N)
      DIMENSION R(3,3),TX(3,3),TY(3,3)
      INTEGER A(4),B(4)
      IF (A(1).LT.B(1)) GO TO 10
      R(1,1)=-R(1,1)
      TX(1,1)=-TX(1,1)
      TY(1,1)=-TY(1,1)
      IF (N.EQ.1) GO TO 5
      R(2,1)=-R(2,1)
      R(3,1)=-R(3,1)
      TX(2,1)=-TX(2,1)
      TX(3,1)=-TX(3,1)
      TY(2,1)=-TY(2,1)
      TY(3,1)=-TY(3,1)
      GO TO 10
   5  R(1,2)=-R(1,2)
      R(1,3)=-R(1,3)
      TX(1,2)=-TX(1,2)
      TX(1,3)=-TX(1,3)
      TY(1,2)=-TY(1,2)
      TY(1,3)=-TY(1,3)
 10   RETURN
      END
C
      SUBROUTINE PERM4T(R,TX,TY,A,B,N)
      DIMENSION R(3,3),TX(3,3),TY(3,3)
      INTEGER A(4),B(4)
      DIMENSION RT(3,3),TXT(3,3),TYT(3,3)
      IF (N.EQ.1) GO TO 10
```

```
      DO 5 I=1,3
      DO 5 J=1,3
      RT(I,J)=R(J,I)
      TXT(I,J)=TX(J,I)
5     TYT(I,J)=TY(J,I)
      GO TO 20
10    DO 15 I=1,3
      DO 15 J=1,3
      RT(I,J)=R(I,J)
      TXT(I,J)=TX(I,J)
15    TYT(I,J)=TY(I,J)
20    IF (A(1).LT.B(1)) GO TO 100
      IF (A(1).LT.B(2)) GO TO 90
      IF (A(1).LT.B(3)) GO TO 80
      DO 50 I=1,3
      R(1,I)=RT(1,I)
      RT(1,I)=RT(3,I)
      RT(3,I)=-R(1,I)
      TX(1,I)=TXT(1,I)
      TXT(1,I)=TXT(3,I)
      TXT(3,I)=-TX(1,I)
      TY(1,I)=TYT(1,I)
      TYT(1,I)=TYT(3,I)
50    TYT(3,I)=-TY(1,I)
      GO TO 100
80    DO 85 I=1,3
      R(1,I)=RT(1,I)
      RT(1,I)=-RT(3,I)
      RT(3,I)=-RT(2,I)
      RT(2,I)=R(1,I)
      TX(1,I)=TXT(1,I)
      TXT(1,I)=-TXT(3,I)
      TXT(3,I)=-TXT(2,I)
      TXT(2,I)=TX(1,I)
      TY(1,I)=TYT(1,I)
      TYT(1,I)=-TYT(3,I)
      TYT(3,I)=-TYT(2,I)
85    TYT(2,I)=TY(1,I)
      GO TO 100
90    DO 95 I=1,3
      RT(1,I)=-RT(1,I)
      R(2,I)=RT(2,I)
      RT(2,I)=RT(3,I)
      RT(3,I)=R(2,I)
      TXT(1,I)=-TXT(1,I)
      TX(2,I)=TXT(2,I)
      TXT(2,I)=TXT(3,I)
      TXT(3,I)=TX(2,I)
      TYT(1,I)=-TYT(1,I)
      TY(2,I)=TYT(2,I)
      TYT(2,I)=TYT(3,I)
95    TYT(3,I)=TY(2,I)
100   IF (N.EQ.1) GO TO 110
      DO 105 I=1,3
      DO 105 J=1,3
      R(I,J)=RT(J,I)
      TX(I,J)=TXT(J,I)
105   TY(I,J)=TYT(J,I)
```

```
      GO TO 120
 110  DO 115 I=1,3
      DO 115 J=1,3
      R(I,J)=RT(I,J)
      TX(I,J)=TXT(I,J)
 115  TY(I,J)=TYT(I,J)
 120  RETURN
      END
C
      SUBROUTINE PERM6T(R,TX,TY,A,B,N)
      DIMENSION R(3,3),TX(3,3),TY(3,3)
      INTEGER A(4),B(4)
      DIMENSION RT(3,3),TXT(3,3),TYT(3,3)
      IF (N.EQ.1) GO TO 10
      DO 5 I=1,3
      DO 5 J=1,3
      RT(I,J)=R(J,I)
      TXT(I,J)=TX(J,I)
 5    TYT(I,J)=TY(J,I)
      GO TO 20
 10   DO 15 I=1,3
      DO 15 J=1,3
      RT(I,J)=R(I,J)
      TXT(I,J)=TX(I,J)
 15   TYT(I,J)=TY(I,J)
 20   IF (A(2).LT.B(1)) GO TO 100
      IF ((A(1).LT.B(1)).AND.(B(1).LT.A(2)).AND.(A(2).LT.B(2))) GO TO 90
      IF ((A(1).LT.B(1)).AND.(B(2).LT.A(2))) GO TO 80
      IF ((B(1).LT.A(1)).AND.(A(2).LT.B(2))) GO TO 70
      IF ((B(1).LT.A(1)).AND.(A(1).LT.B(2)).AND.(B(2).LT.A(2))) GO TO 60
      DO 55 I=1,3
      RT(1,I)=-RT(1,I)
      RT(3,I)=-RT(3,I)
      TXT(1,I)=-TXT(1,I)
      TXT(3,I)=-TXT(3,I)
      TYT(1,I)=-TYT(1,I)
 55   TYT(3,I)=-TYT(3,I)
      GO TO 100
 60   DO 65 I=1,3
      R(1,I)=RT(1,I)
      RT(1,I)=-RT(2,I)
      RT(2,I)=R(1,I)
      TX(1,I)=TXT(1,I)
      TXT(1,I)=-TXT(2,I)
      TXT(2,I)=TX(1,I)
      TY(1,I)=TYT(1,I)
      TYT(1,I)=-TYT(2,I)
 65   TYT(2,I)=TY(1,I)
      GO TO 100
 70   DO 75 I=1,3
      R(1,I)=RT(1,I)
      RT(1,I)=RT(2,I)
      RT(2,I)=-RT(3,I)
      RT(3,I)=-R(1,I)
      TX(1,I)=TXT(1,I)
      TXT(1,I)=TXT(2,I)
      TXT(2,I)=-TXT(3,I)
      TXT(3,I)=-TX(1,I)
```

```
      TY(1,I)=TYT(1,I)
      TYT(1,I)=TYT(2,I)
      TYT(2,I)=-TYT(3,I)
 75   TYT(3,I)=-TY(1,I)
      GO TO 100
 80   DO 85 I=1,3
      R(1,I)=RT(1,I)
      RT(1,I)=RT(2,I)
      RT(2,I)=RT(3,I)
      RT(3,I)=R(1,I)
      TX(1,I)=TXT(1,I)
      TXT(1,I)=TXT(2,I)
      TXT(2,I)=TXT(3,I)
      TXT(3,I)=TX(1,I)
      TY(1,I)=TYT(1,I)
      TYT(1,I)=TYT(2,I)
      TYT(2,I)=TYT(3,I)
 85   TYT(3,I)=TY(1,I)
      GO TO 100
 90   DO 95 I=1,3
      R(1,I)=RT(1,I)
      RT(1,I)=-RT(2,I)
      RT(2,I)=-R(1,I)
      RT(3,I)=-RT(3,I)
      TX(1,I)=TXT(1,I)
      TXT(1,I)=-TXT(2,I)
      TXT(2,I)=-TX(1,I)
      TXT(3,I)=-TXT(3,I)
      TY(1,I)=TYT(1,I)
      TYT(1,I)=-TYT(2,I)
      TYT(2,I)=-TY(1,I)
 95   TYT(3,I)=-TYT(3,I)
 100  IF (N.EQ.1) GO TO 110
      DO 105 I=1,3
      DO 105 J=1,3
      R(I,J)=RT(J,I)
      TX(I,J)=TXT(J,I)
 105  TY(I,J)=TYT(J,I)
      GO TO 120
 110  DO 115 I=1,3
      DO 115 J=1,3
      R(I,J)=RT(I,J)
      TX(I,J)=TXT(I,J)
 115  TY(I,J)=TYT(I,J)
 120  RETURN
      END
C
      SUBROUTINE PERM12T(R,TX,TY,A,B,C,N)
      DIMENSION R(3,3),TX(3,3),TY(3,3)
      INTEGER A(4),B(4),C(4)
      DIMENSION RT(3,3),TXT(3,3),TYT(3,3)
      IF (N.EQ.1) GO TO 10
      DO 5 I=1,3
      DO 5 J=1,3
      RT(I,J)=R(J,I)
      TXT(I,J)=TX(J,I)
 5    TYT(I,J)=TY(J,I)
      GO TO 20
```

```
10    DO 15 I=1,3
      DO 15 J=1,3
      RT(I,J)=R(I,J)
      TXT(I,J)=TX(I,J)
15    TYT(I,J)=TY(I,J)
20    IF ((A(1).LT.B(1)).AND.(B(1).LT.C(1))) GO TO 200
      IF ((B(1).LT.A(1)).AND.(A(1).LT.C(1))) GO TO 190
      IF ((A(1).LT.B(1)).AND.(A(1).GT.C(1)).AND.(B(1).LT.C(2))) GOTO 180
      IF ((B(1).LT.A(1)).AND.(B(1).GT.C(1)).AND.(A(1).LT.C(2))) GOTO 170
      IF ((A(1).LT.B(1)).AND.(A(1).GT.C(2))) GO TO 160
      IF ((B(1).LT.A(1)).AND.(B(1).GT.C(2))) GO TO 150
      IF ((A(1).LT.C(1)).AND.(C(1).LT.B(1)).AND.(B(1).LT.C(2))) GOTO 140
      IF ((B(1).LT.C(1)).AND.(C(1).LT.A(1)).AND.(A(1).LT.C(2))) GOTO 130
      IF ((A(1).LT.C(1)).AND.(C(2).LT.B(1))) GO TO 120
      IF ((B(1).LT.C(1)).AND.(C(2).LT.A(1))) GO TO 110
      IF ((C(1).LT.A(1)).AND.(A(1).LT.C(2)).AND.(C(2).LT.B(1))) GOTO 100
      DO 95 I=1,3
      R(1,I)=RT(1,I)
      RT(1,I)=-RT(3,I)
      RT(3,I)=RT(2,I)
      RT(2,I)=-R(1,I)
      TX(1,I)=TXT(1,I)
      TXT(1,I)=-TXT(3,I)
      TXT(3,I)=TXT(2,I)
      TXT(2,I)=-TX(1,I)
      TY(1,I)=TYT(1,I)
      TYT(1,I)=-TYT(3,I)
      TYT(3,I)=TYT(2,I)
95    TYT(2,I)=-TY(1,I)
      GO TO 200
100   DO 105 I=1,3
      R(1,I)=RT(1,I)
      RT(1,I)=-RT(2,I)
      RT(2,I)=R(1,I)
      TX(1,I)=TXT(1,I)
      TXT(1,I)=-TXT(2,I)
      TXT(2,I)=TX(1,I)
      TY(1,I)=TYT(1,I)
      TYT(1,I)=-TYT(2,I)
105   TYT(2,I)=TY(1,I)
      GO TO 200
110   DO 115 I=1,3
      R(1,I)=RT(1,I)
      RT(1,I)=RT(3,I)
      RT(3,I)=-R(1,I)
      TX(1,I)=TXT(1,I)
      TXT(1,I)=TXT(3,I)
      TXT(3,I)=-TX(1,I)
      TY(1,I)=TYT(1,I)
      TYT(1,I)=TYT(3,I)
115   TYT(3,I)=-TY(1,I)
      GO TO 200
120   DO 125 I=1,3
      R(1,I)=RT(1,I)
      RT(1,I)=RT(2,I)
      RT(2,I)=RT(3,I)
      RT(3,I)=R(1,I)
      TX(1,I)=TXT(1,I)
```

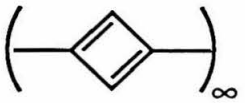
```
      TXT(1,I)=TXT(2,I)
      TXT(2,I)=TXT(3,I)
      TXT(3,I)=TX(1,I)
      TY(1,I)=TYT(1,I)
      TYT(1,I)=TYT(2,I)
      TYT(2,I)=TYT(3,I)
125   TYT(3,I)=TY(1,I)
      GO TO 200
130   DO 135 I=1,3
      R(1,I)=RT(1,I)
      RT(1,I)=-RT(3,I)
      RT(3,I)=-RT(2,I)
      RT(2,I)=R(1,I)
      TX(1,I)=TXT(1,I)
      TXT(1,I)=-TXT(3,I)
      TXT(3,I)=-TXT(2,I)
      TXT(2,I)=TX(1,I)
      TY(1,I)=TYT(1,I)
      TYT(1,I)=-TYT(3,I)
      TYT(3,I)=-TYT(2,I)
135   TYT(2,I)=TY(1,I)
      GO TO 200
140   DO 145 I=1,3
      R(1,I)=RT(1,I)
      RT(1,I)=-RT(2,I)
      RT(2,I)=-R(1,I)
      RT(3,I)=-RT(3,I)
      TX(1,I)=TXT(1,I)
      TXT(1,I)=-TXT(2,I)
      TXT(2,I)=-TX(1,I)
      TXT(3,I)=-TXT(3,I)
      TY(1,I)=TYT(1,I)
      TYT(1,I)=-TYT(2,I)
      TYT(2,I)=-TY(1,I)
145   TYT(3,I)=-TYT(3,I)
      GO TO 200
150   DO 155 I=1,3
      R(2,I)=RT(2,I)
      RT(2,I)=RT(3,I)
      RT(3,I)=-R(2,I)
      TX(2,I)=TXT(2,I)
      TXT(2,I)=TXT(3,I)
      TXT(3,I)=-TX(2,I)
      TY(2,I)=TYT(2,I)
      TYT(2,I)=TYT(3,I)
155   TYT(3,I)=-TY(2,I)
      GO TO 200
160   DO 165 I=1,3
      RT(1,I)=-RT(1,I)
      RT(3,I)=-RT(3,I)
      TXT(1,I)=-TXT(1,I)
      TXT(3,I)=-TXT(3,I)
      TYT(1,I)=-TYT(1,I)
165   TYT(3,I)=-TYT(3,I)
      GO TO 200
170   DO 175 I=1,3
      R(1,I)=RT(1,I)
      RT(1,I)=RT(3,I)
```

```
      RT(2,I)=-RT(2,I)
      RT(3,I)=R(1,I)
      TX(1,I)=TXT(1,I)
      TXT(1,I)=TXT(3,I)
      TXT(2,I)=-TXT(2,I)
      TXT(3,I)=TX(1,I)
      TY(1,I)=TYT(1,I)
      TYT(1,I)=TYT(3,I)
      TYT(2,I)=-TYT(2,I)
175   TYT(3,I)=TY(1,I)
      GO TO 200
180   DO 185 I=1,3
      R(1,I)=RT(1,I)
      RT(1,I)=RT(2,I)
      RT(2,I)=-RT(3,I)
      RT(3,I)=-R(1,I)
      TX(1,I)=TXT(1,I)
      TXT(1,I)=TXT(2,I)
      TXT(2,I)=-TXT(3,I)
      TXT(3,I)=-TX(1,I)
      TY(1,I)=TYT(1,I)
      TYT(1,I)=TYT(2,I)
      TYT(2,I)=-TYT(3,I)
185   TYT(3,I)=-TY(1,I)
      GO TO 200
190   DO 195 I=1,3
      RT(1,I)=-RT(1,I)
      R(2,I)=RT(2,I)
      RT(2,I)=RT(3,I)
      RT(3,I)=R(2,I)
      TXT(1,I)=-TXT(1,I)
      TX(2,I)=TXT(2,I)
      TXT(2,I)=TXT(3,I)
      TXT(3,I)=TX(2,I)
      TYT(1,I)=-TYT(1,I)
      TY(2,I)=TYT(2,I)
      TYT(2,I)=TYT(3,I)
195   TYT(3,I)=TY(2,I)
200   IF (N.EQ.1) GO TO 210
      DO 205 I=1,3
      DO 205 J=1,3
      R(I,J)=RT(J,I)
      TX(I,J)=TXT(J,I)
205   TY(I,J)=TYT(J,I)
      GO TO 220
210   DO 215 I=1,3
      DO 215 J=1,3
      R(I,J)=RT(I,J)
      TX(I,J)=TXT(I,J)
215   TY(I,J)=TYT(I,J)
220   RETURN
      END
```

Chapter 3

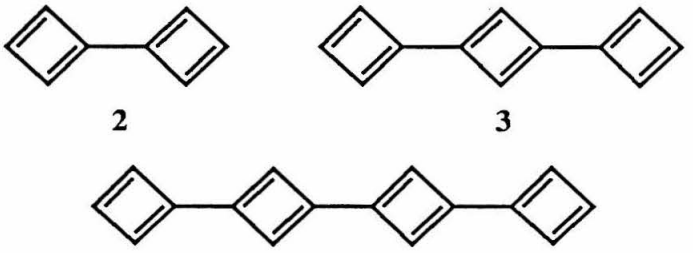
Bi(cyclobutadienyl) and Its Higher Homologues

A natural extension of our study of the non-Kekulé acenes (Chapter 2) is to consider what happens when the number of "monomers" gets to be infinitely large. In "non-Kekulé polyacene", the effects of the methylene end groups must become negligible, and one is left with polycyclobutadiene (**1**).



1

Before considering **1** itself, however, we undertook a detailed theoretical study of the smaller, finite structures related to it, specifically bi-, tri-, and tetra(cyclobutadienyl) (**2**–**4**).



2 **3**

4

The first member of this homologous series is cyclobutadiene, which has, of course, been extensively studied as the prototype of antiaromaticity.[1] Structure **2** is related to cyclobutadiene the way biphenyl is related to benzene, yet, surprisingly, only a few studies have appeared that mention **2**.[2] We could find no reference to **3** or **4** in the literature.

Structures **2**–**4**, and all higher homologues, are alternant hydrocarbons. Unlike the non-Kekulé acenes, no "parity rule" is in effect here. All members of the poly(cyclobutadienyl) series have equal numbers of starred and unstarred atoms. Thus, all are expected to have singlet ground states. With regard to classical structure theory, no member of the series is non-Kekulé; all can be represented (as shown above) as a chain of cyclobutadienes. Thus, classical structure theory also predicts singlet ground states. However, Hückel theory predicts the existence of two NBMOs for **2** (and for

cyclobutadiene), and four for **3** and **4**; the same number as for the analogous non-Kekulé acenes. Coupled with Hund's rule, this predicts high spin ground states for this series of molecules. Although the applicability of Hund's rule for these kinds of systems is by no means universal (as we have shown in Chapter 2), we might expect the presence of low-lying excited states to be a characteristic of this series of molecules. In the present work, we explore these factors as well as the geometrical preferences of structures **2**–**4**. Producing quantitatively reliable results for structures with many NBMOs presents a substantial theoretical challenge[3] and is not the goal of the present work. Rather, we seek a qualitative understanding of the molecular and electronic structure of these molecules. However, a fairly high level of theory is required even to achieve this more modest goal.

General Considerations

Bi(cyclobutadienyl) (**2**) is a biradical, in the sense that it has two NBMOs. As discussed in Chapter 1, for such structures one needs at least a two-configuration (TCSCF) wave function to describe the singlet state properly. The triplet state may be adequately described by a single configuration RHF wave function. However, further complications arise because **2** is a *conjugated* biradical. Borden and co-workers have demonstrated that for such structures, the RHF/TCSCF levels of theory may not be adequate.[4] The reason is related to the "doublet instability problem" such as found in allyl radical.[5–7]

The problem is illustrated in Figure 1, which shows the bonding and nonbonding π MOs of allyl radical. In an RHF wave function (Fig. 1, a), the bonding orbital is doubly occupied. There are large coefficients at the end carbons in *both* the bonding and the nonbonding orbital. The nonbonding electron and the bonding electron having the opposite spin can simultaneously occupy the same atomic orbital (AO), giving rise to high-energy ionic terms in the wave function. (Such a situation does not occur with the

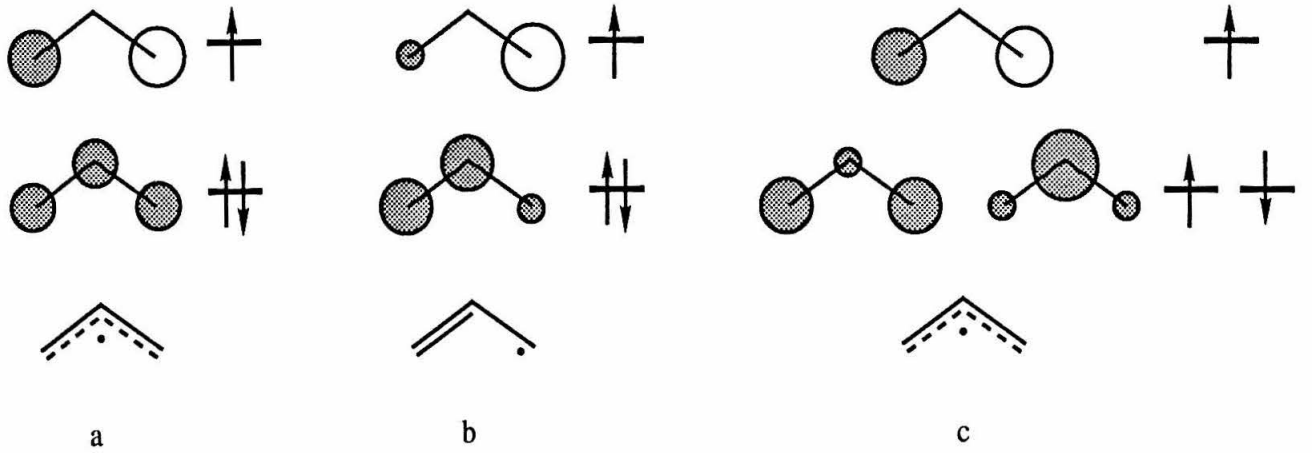


Figure 1. The doublet instability problem in allyl radical (see text for details). (a) Situation giving rise to the problem. (b) Incorrect RHF solution. (c) Correct UHF solution.

other bonding electron, since its spin is parallel to the nonbonding electron's, and thus the Pauli principle keeps them from simultaneously occupying the same AO.)

In order to minimize this electron–electron repulsion, an RHF wave function distorts the MOs to the form shown in Figure 1b. The two bonding electrons are localized in a bond at one end of the molecule, while the nonbonding electron is spatially far away at the other end. Geometry optimizations of allyl radical using the RHF method incorrectly result in unequal CC bond lengths.[5–7]

The correct solution to the doublet instability problem is through spin polarization. This is illustrated, in the language of UHF theory,[8] in Figure 1c. The nonbonding electron causes the bonding electron having opposite spin to be more localized at the central atom. This causes the other bonding electron to be more localized at the end atoms. Although *on average* it now occupies the same AOs as the nonbonding electron, the Pauli principle keeps them from *simultaneously* appearing in the same AO. Thus, electron–electron repulsions are minimized. This solution is not possible within the framework of RHF theory, since RHF does not permit different spatial orbitals for the two bonding electrons. Geometry optimizations of allyl radical using UHF theory result in the correct symmetric structure, with equal CC bond lengths.[6]

Another way to overcome the doublet instability problem is through the use of a configuration interaction (CI) wave function.[7] The problem is essentially one of correlation between the nonbonding electron and the bonding electron having opposite spin, and CI is one method of improving electron correlation.

As shown by Borden and co-workers, RHF or TCSCF wave functions for conjugated biradicals also suffer from inadequate correlation between electrons in the NBMO and electrons in the lower-lying MOs.[4] As in allyl radical, a solution can be found by using UHF or CI methods. The problem with the UHF method is that it does not result in a pure spin eigenfunction. Furthermore, UHF can be used only for the triplet

state, and an analogous calculation that can be directly compared to the UHF triplet cannot be performed for the singlet state, making predictions about singlet–triplet gaps impossible. On the other hand, CI calculations are computationally more difficult and costly, especially when geometry optimizations are involved.

As a compromise, we used the UHF method for geometry optimizations on **2–4**. These optimizations were performed on the high-spin states suggested by Hund's rule; i.e., triplet for **2** and quintet for **3** and **4**. At least for biradicals, the geometry calculated by this method is a reasonable approximation of the geometry obtained by π-CI calculations.[4] At the UHF-optimized geometries, we performed CI calculations to determine the relative energies of the various spin states. However, we also performed geometry optimizations using the RHF method, in order to demonstrate the inadequacy of this method for this type of molecules.

Computational Methods

Bi(cyclobutadienyl) (**2**) was studied using ab initio molecular orbital theory. Geometry optimizations were performed using the STO-3G basis set,[9] and more refined energy calculations, including CI, were performed using the 4-31G basis set.[10] These levels of theory are not "state of the art", and we have chosen them in order to minimize the computational requirements. As such, they are probably inadequate for quantitatively accurate results, but we believe these calculations predict the qualitative trends correctly.

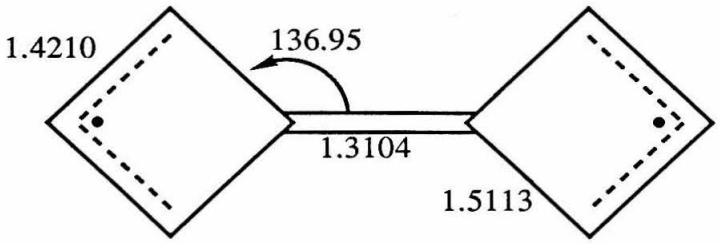
SCF calculations (RHF, UHF, TCSCF) were performed using the Gaussian 86 program package.[11] The CI calculations were restricted to orbitals of π symmetry, and only the eight orbitals corresponding to a conceptual minimum basis set were included. All possible configurations within this set of orbitals were included in the CI. Molecular orbitals for CI calculations were optimized at the RHF level for triplet states and the

TCSCF level for singlets (using Gaussian 86). The CI calculations themselves were performed using the MQM:CI2P5 program.[12]

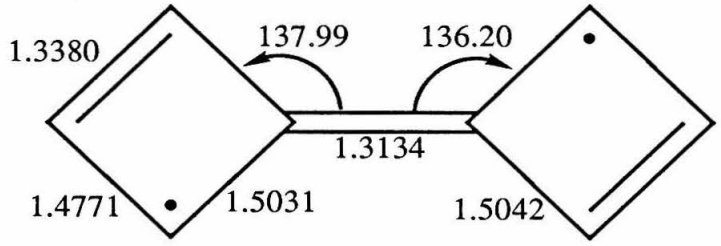
Because of their larger size, ab initio calculations comparable to those for **2** are infeasible for **3** and **4**. We studied these structures using the semiempirical MNDO method.[13] Most of the MNDO calculations were performed using the AMPAC program;[14] because of the limited UHF capability of AMPAC, the UHF calculations were performed using Gaussian 86. MNDO calculations were also performed for **2**, primarily for comparison with the ab initio results, in order to assess the performance of this semiempirical method for this series of molecules. Since AMPAC does not allow TCSCF calculations, singlet energies comparable to TCSCF energies were obtained by specifying two NBMOs and performing CI calculations within the NBMOs.

Bi(cyclobutadienyl)

Geometries. The geometries optimized using UHF (**2a**) and RHF (**2b**) methods for the triplet state are shown in Figure 2, and energies of these structures at various levels of theory are shown in Table I. These geometries clearly indicate that **2** is best represented as two allyl radicals plus an ethylene. In other words, there is a double bond between the two four-membered rings. The same conclusion was reached by Iwamura and Hoffmann from PPP–SCF–CI calculations.[2b] In contrast, the central bond in biphenyl is clearly a single bond; in the gas phase, the two rings are twisted 42° around this bond, and the bond length is 1.489 Å.[15] Another significant difference from biphenyl is in the structure of the rings themselves. In biphenyl, each ring is essentially a benzene ring, whereas in **2** the rings do *not* have a cyclobutadiene structure. Such a "classical" structure *can* be obtained, provided the geometry optimization is performed on an RHF *singlet* (**2c**, Figure 2),[16] which forces all the electrons to be paired. In this case, the



2a



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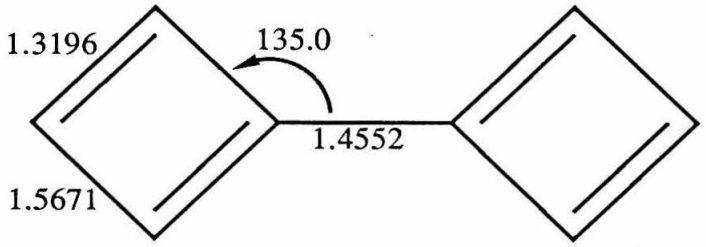


2c

Figure 2. Optimized structures for bi(cyclobutadienyl). Bond lengths in angstroms, angles in degrees. **2a**: UHF triplet. The structure was fully optimized within D_{2h} symmetry, following a partial optimization within C_{2h} symmetry, which led to a D_{2h} structure. Frequency calculations show this structure to be a true minimum. **2b**: RHF triplet. The structure was partially optimized (hydrogen positions not optimized) within C_{2h} symmetry. **2c**: RHF singlet. Only CC bond lengths were optimized, and the rings were constrained to be rectangular.

Table I. Energies of structures **2a**, **2b**, and **2c** (a.u.).

	2a[a]	**2b**	**2c**[b]
Triplet			
RHF/STO-3G	−302.427453	−302.443348	−302.344666
RHF/4-31G	−305.734695	−305.738786	
π-CI/4-31G	−305.831344	−305.821868	
Singlet			
TCSCF/STO-3G	−302.427467	−302.444206	−302.408227
TCSCF/4-31G	−305.734887	−305.739949	
π-CI/4-31G	−305.833126	−305.824634	

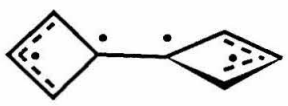
[a]Triplet UHF/STO-3G energy = −302.505710 a.u. [b]Singlet RHF/STO-3G energy = −302.379478 a.u.[16]

central bond is longer, though still short for a single bond. However, as shown in Table I, the energy of this structure is higher than **2a** or **2b**, especially for the triplet state.

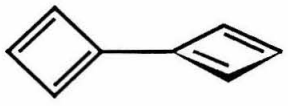
The inadequacy of the RHF method for geometry optimizations is reflected in the energies shown in Table I: At the highest level of theory (i.e., π-CI), the more symmetrical, UHF-optimized structure (**2a**) is preferred. (However, the energy difference from the RHF structure (**2b**) is only ca. 6 kcal/mol.) In **2a**, the two allyl fragments have equal CC bond lengths, as expected for a free allyl radical. In **2b**, the CC bond lengths are unequal, the same problem experienced by RHF for allyl radical. In spite of the incorrect geometry, the RHF/TCSCF method does predict the same ordering of singlet and triplet states as the π-CI calculations. All levels of theory predict the singlet to be the ground state, with the triplet being a low-lying excited state. However, the difference is quite small, and given the uncertainties of the calculations , perhaps it is best to say than the singlet and triplet states are essentially degenerate.

Rotation Barriers. The existence of a double bond between the two rings indicates that **2** strongly prefers a planar structure. This was further confirmed when we performed calculations to estimate the rotation barrier around this bond. Two structures were considered. In **2d**, we simply rotate the rings until they are perpendicular to each other, keeping the geometry of the rings at the UHF-optimized values (those of **2a**). As this would obviously break the exocyclic π bond, the bond length was increased to 1.48 Å. Structure **2d** is a tetraradical, formed by a spiro-fusion of two biradicals. In earlier studies it has been shown that an adequate level of theory for such structures is to optimize the molecular orbitals for a quintet state using RHF, followed by a CI calculation within the full NBMO-space to obtain energies of the singlet and triplet states.[17] For **2d**, we also performed a larger CI calculation, including the eight orbitals that formerly had π symmetry in the planar structure. Although some σ–π mixing occurs in the perpendicular structure, it turns out that the "π" type orbitals are quite easy to identify. This type of CI

calculation would allow meaningful energy comparisons to the planar structure. The energies of structure **2d**, at the various levels of theory for the various states, are shown in Table II.



2d



2e

The other structure we considered is **2e**, which is simply two mutually perpendicular, rectangular cyclobutadienes. The cyclobutadiene geometry used was the one reported by Borden and co-workers, which was obtained at the π-CI level using a minimum basis set (r_{C-C} = 1.539 Å, $r_{C=C}$ = 1.369Å).[1a] The central bond was again assumed to be 1.48 Å. There is some uncertainty as to what level of theory would be adequate for **2e**. TCSCF calculations on singlet cyclobutadiene at this geometry results in CI coefficients of 0.9543 and −0.2990 for the two configurations. The energy at this level of theory is −153.417345 a.u. Clearly, one configuration is dominant. When the calculation is done at the RHF level, followed by a CI calculation consisting of only two configurations (the two configurations in the TCSCF wave function), the CI coefficients are 0.9600 and −0.2800, and the energy is −153.414296 a.u. The difference in energies is less than 2 kcal/mol, and the differences in the CI coefficients are likewise minimal. Thus, the singlet RHF MOs of cyclobutadiene very closely approximate those obtained from a TCSCF calculation. Since the two rings are perpendicular in **2e**, there is essentially no interaction (other than weak spiroconjugation) between the frontier orbitals of the two cyclobutadiene fragments. We conclude that RHF on the singlet state is an adequate method to obtain the orbitals of **2e**. To obtain energies comparable to the other structures, "π"-CI calculations are, of course, necessary. The same type of "π"-CI calculations as performed for **2d** was thus performed for **2e** also. The state energies are shown in Table II. There is, of course, some uncertainty as to the accuracy of these

Table II. Energies of structures **2d** and **2e** (a.u.).

	2d	**2e**
Quintet		
RHF/4-31G	−305.674696	
π-CI/4-31G	−305.729835	−305.653887
Triplet		
NBMO-CI/4-31G	−305.671228	
π-CI/4-31G	−305.742839	−305.698498
Singlet		
RHF/4-31G		−305.657494
NBMO-CI/4-31G	−305.669715	
π-CI/4-31G	−305.753839	−305.739129

energies, given that they are not calculated for optimized structures. However, they are quite significantly (ca. 50 kcal/mol) above the energies of the planar structure. We conclude that **2** strongly prefers the planar geometry. It is remarkable that at least computationally, tetraradical **2d** is more stable than "closed-shell" **2e**, a real testimony to the destabilization of a cyclobutadiene ring.

Electronic Transitions. We have also calculated the energies of the higher-lying singlet and triplet states of **2**, at the geometry of **2a**. These were obtained by CI calculations from the same orbitals optimized for the ground state (RHF for triplets, TCSCF for singlets). These are still relatively crude calculations for excited states, but should provide useful guidelines. The results are shown in Table III.

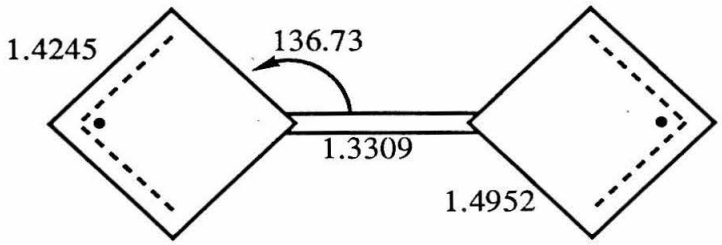
Unfortunately, the calculations indicate that *both* the triplet and singlet states have absorptions at about 410 nm. Thus, UV-vis spectroscopy is not expected to be able to distinguish between these two spin states, an observation of considerable importance to experimental efforts to prepare **2**.

MNDO Calculations. As mentioned in the previous section, we also performed MNDO calculations on **2**, mainly for comparison to the ab initio results. Qualitatively, the MNDO results are the same as the results obtained from ab initio calculations: RHF incorrectly predicts unsymmetric allyl fragments, whereas UHF predicts symmetric allyls (Figure 3). At both geometries, the singlet and triplet states are essentially degenerate (Table IV).

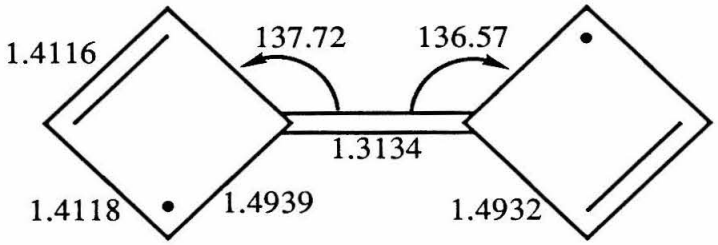
All levels of ab initio theory predict the singlet and triplet states of **2** to be essentially degenerate. The same result is obtained with MNDO, using RHF for the triplet and NBMO-CI for the singlet (i.e., *without* full π-CI). Thus, once the correct geometry is obtained by UHF, a full π-CI calculation is not necessary; it is sufficient to perform the CI calculations within the NBMOs.

Table III. Calculated electronic transitions for **2.**

	Wavelength (nm)
Triplet transitions	
$B_{1u} \rightarrow B_{3g}$ (allowed)	410.6
$B_{1u} \rightarrow A_g$ (allowed)	401.4
$B_{1u} \rightarrow A_g$ (allowed)	401.3
$B_{1u} \rightarrow B_{2u}$ (forbidden)	400.9
Singlet transitions	
$A_g \rightarrow B_{3g}$ (forbidden)	426.6
$A_g \rightarrow B_{2u}$ (allowed)	411.2
$A_g \rightarrow A_g$ (forbidden)	374.7
$A_g \rightarrow B_{3g}$ (forbidden)	236.5



2f



2g

Figure 3. MNDO-optimized structures for bi(cyclobutadienyl). Bond lengths in angstroms, angles in degrees. **2f**: UHF triplet (D_{2h}). **2g**: RHF triplet (C_{2h}). Both structures were partially optimized within C_{2h} symmetry. Hydrogen positions were not optimized.

Table IV. MNDO heats of formation (kcal/mol).

	Singlet	Triplet	Quintet
2f	158.840	158.841	
2g	158.412	158.416	
3a	239.398	239.344	239.318
3b	312.468		
4a	310.373	310.373	319.380
4b	312.538	312.538	312.538

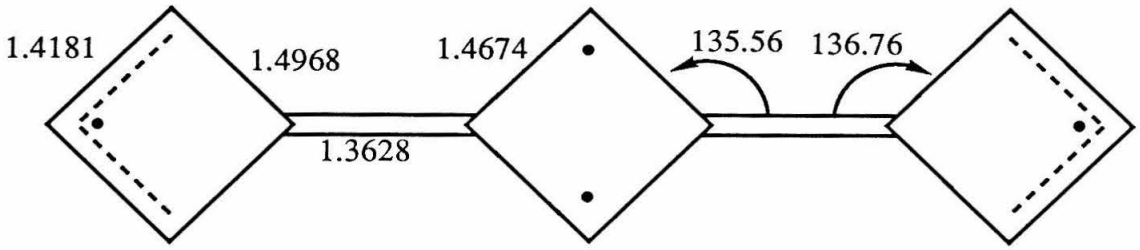
Tri(cyclobutadienyl) and Tetra(cyclobutadienyl)

HMO calculations on **3** and **4** predict the existence of four NBMOs for each structure. Thus, a UHF *quintet* calculation is necessary to obtain the correct geometry. Relative energies of the singlet, triplet, and quintet states can then be obtained from CI calculations within the NBMO space. These calculations were performed using the MNDO method.[13]

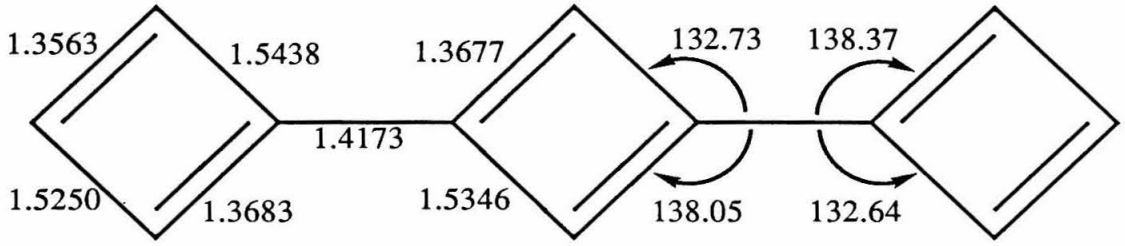
The UHF-optimized geometry (**3a**) is shown in Figure 4, and the energies (in the form of heats of formation), in Table IV. These energies were obtained by NBMO-CI using the RHF-quintet optimized orbitals. The singlet, triplet, and quintet states are essentially degenerate, and clearly the molecule is best thought of as a tetraradical.[17] It is worthwhile to note that like **2**, **3** does not undergo a distortion towards rectangular cyclobutadiene structures. Optimization of **3** as an RHF *singlet* does lead to such a structure (**3b**, Figure 4); however, the energy (obtained by CI calculations within the two highest occupied and the two lowest unoccupied MOs, corresponding to the four NBMOs in **3a**) for this structure is much higher (about 70 kcal/mol) than the energy for **3a** (Table IV).

For **4**, the optimized (UHF quintet) geometry (**4a**) is shown in Figure 5. Energies are shown in Table IV. Once again, the singlet, triplet, and quintet states are essentially degenerate, and the molecule is a tetraradical.

A feature in **4** not seen in **2** or **3** is an exocyclic *single* bond between the middle rings. Although the bond length indicates some partial double bond character, it is still substantially longer than the exocyclic bonds in **2** and **3**, and the other two exocyclic bonds in **4** itself. We performed further calculations on **4**, assuming a perpendicular orientation of the two fragments around this bond (**4b**, Table IV). The results indicate that the rotation barrier is only about 2 kcal/mol, much smaller than the rotation barrier in **2**, but the planar structure is still preferred.[18]

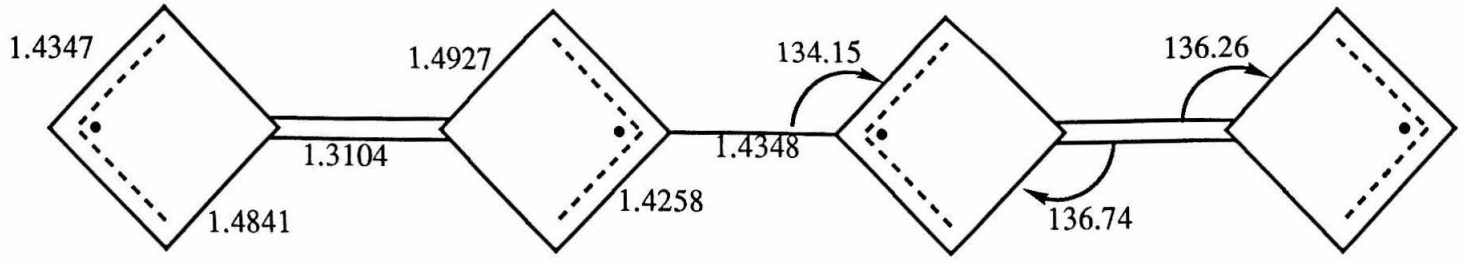


3a



3b

Figure 4. MNDO-optimized structures for tri(cyclobutadienyl). Bond lengths in angstroms, angles in degrees. **3a**: UHF quintet. The structure was fully optimized within D_{2h} symmetry, following a partial optimization within C_{2h} symmetry, which led to the D_{2h} structure. **3b**: RHF singlet. The structure was fully optimized within C_{2h} symmetry.



4a

Figure 5. MNDO-optimized structure for tetra(cyclobutadienyl). Bond lengths in angstroms, angles in degrees. The structure was optimized as a UHF quintet within D_{2h} symmetry.

Polycyclobutadiene

Our calculations predict a near degeneracy of the various spin states in **2**, **3**, and **4**. If this trend continues, the infinite homologue polycyclobutadiene (**1**) would be a very interesting material. Unfortunately, at the present time we are unable to investigate polymers with open shells with any confidence. Nevertheless, we have performed band structure calculations on **1**, using a variety of methods: simple Hückel molecular orbital (HMO) theory,[20] the extended Hückel crystal orbital (EHCO) method,[21] and the valence effective hamiltonian (VEH) method.[22,23] We emphasize that all these methods were developed for "ordinary", closed-shell polymers, and their results for **1** must be regarded as tentative at best.

The fundamental properties of the band structure of **1** are illustrated in the HMO band structure, shown in Figure 6. Along with a low-lying, completely filled band and a high-lying empty band, there are two bands of intermediate energy that cross (Figure 6, a). The origin of these middle bands is easily deduced. They both arise from the NBMOs of cyclobutadiene, shown in Figure 7. The band that shows a considerable dispersity (i.e., ranges from 1.00 to -1.00 β) results from the left NBMO of Figure 7, which produces significant intercell interactions. The fully "in-phase" combination of this orbital (k=0) has only antibonding intercell interactions and is thus the energy maximum of the band (Figure 6, a). The other band is completely degenerate (zero dispersity) and arises from the right NBMO of Figure 7. There is no dispersion in this band, because at the HMO level, there are no intercell interactions. (Of course, this band is just the infinite extension of the n degenerate NBMOs of the non-Kekulé acenes for even n.)

The band structure in Figure 6a is quite extraordinary. First, there is the presence of an infinitely narrow, half-filled band at the Fermi level. This is an example of "superdegeneracy", a notion recently developed by Hughbanks.[24] The presence of such a band at the Fermi level is typical of "nonclassical polymers";[25] however, **1** certainly does

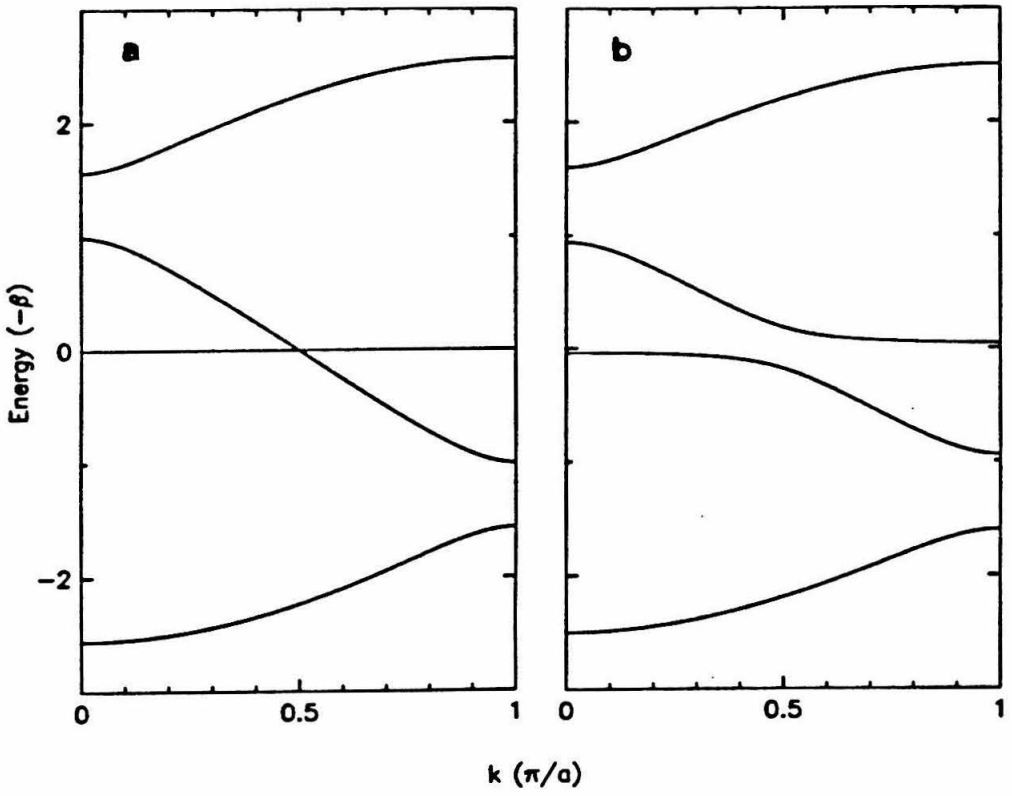


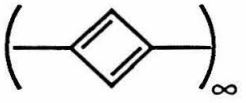
Figure 6. HMO band structure of polycyclobutadiene: (a) regular (all bond integrals equal); (b) with bond alternation.

Figure 7. NBMOs of cyclobutadiene.

not belong in this class. Second, there is a crossing between the valence and conduction bands. Such crossings are rare, and when seen, typically occur very near the zone edge.[21b,26] We are unaware of any system with a crossing at $k=\pi/2a$, as in Figure 6a, or even nearly as far back toward the center of the Brillouin zone.

In Figure 6a, we have assumed, as is common in HMO, that all the bond integrals are identical. However, **1** may adopt a bond-alternating form (such as seen in polyacetylene), with rectangular cyclobutadiene units. One way to model this, within the framework of HMO theory, is to set the bond integrals to 1.1β for double bonds and 0.9β for single bonds (including the intercell connections). This gives the band structure shown in Figure 6b. The lowest and highest bands are barely affected, but the NBMOs of Figure 7 mix, and the crossing between the middle bands is avoided. Even with this distortion, the band structure is very intriguing with a narrow band gap,[27] a high-lying Fermi level, and relatively broad valence and conduction bands. We decided that higher-level, more quantitative calculations on **1** are worthwhile.

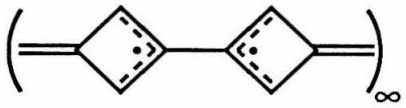
For the EHCO and VEH calculations, three geometries were considered. In **1a**, we have assumed that the unit cell is a rectangular cyclobutadiene (i.e., as assumed in Figure 6b). We have used the middle ring of structure **3b** to approximate the structural parameters of the polymer. This is the "intuitive" structure of **1**: rectangular rings would be expected if one considers the monomer. In addition, the HMO results indicate that this distortion towards rectangular rings open up a band gap, which generally stabilizes closed shell structures.



1a

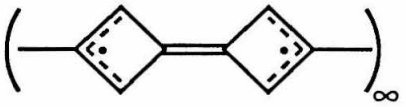
However, *none* of the smaller oligomers we investigated show any tendency towards this type of structure. Thus, other structures must be considered, and **1b** is a sensible choice. The structure is obtained from the two middle rings of **4a**, and

essentially consists of allyl radicals and ethylenes. It appears to be the structure that maximizes bonding without forming antiaromatic cyclobutadiene units.



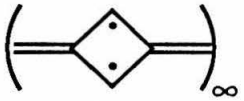
1b

In the infinite polymer, there is an equivalent structure **1b'**. This situation is reminiscent of the two degenerate but distinct structures seen in polyacetylene.



1b'

This suggests an additional form, which would be best represented by **1c**, and which is analogous to polyacetylene with all equal bond lengths. The geometry of **1c** may be approximated by the middle ring of **3a**.



1c

The results of the band structure calculations on **1a**–**1c** are shown in Table V and Figure 8. EHCO is used to obtain the energies, and VEH, to obtain the other parameters. The VEH band structures are shown in Figure 8. EHCO band structures are similar.

The calculations indicate no clear preference for any of the three structures we considered. Although **1a** is calculated to be slightly lower in energy, this is to be expected since **1a** is the best representation of a closed-shell structure, and the calculations are biased in favor of such structures. Thus, structures **1b** and **1c**, which have zero band gaps, cannot be ruled out as the ground state structure of polycyclobutadiene.

The band structures obtained by EHCO and VEH methods are in complete agreement with the HMO results. There is a crossing (avoided in **1a**, but allowed in the higher symmetry **1c**) between the valence and conduction bands. In **1b**, the potential

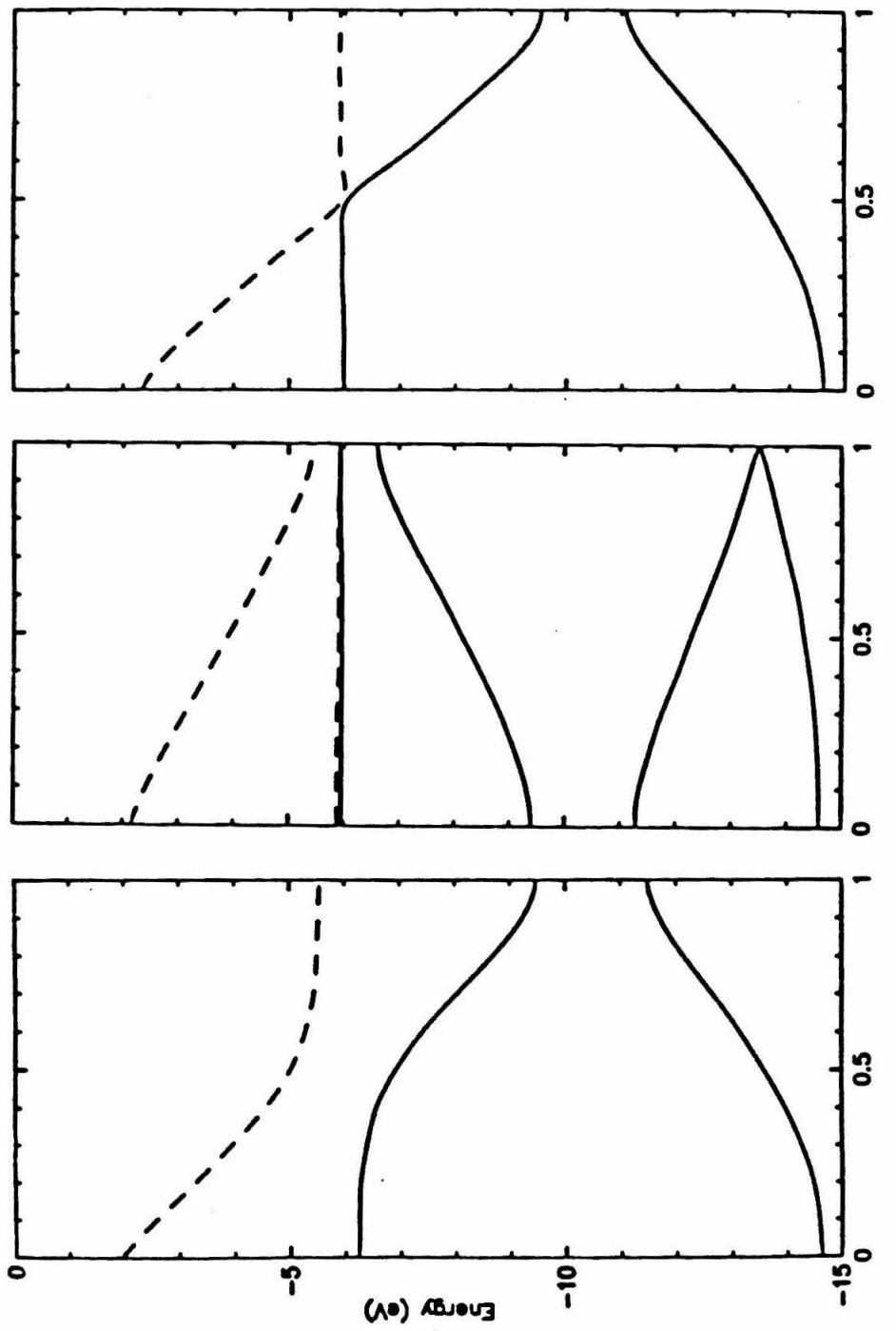


Figure 8. VEH band structures of **1a** (left), **1b** (middle), and **1c** (right). Unoccupied bands are shown as dashes. **1b** has a greater number of bands due to its larger unit cell.

Table V. Results of EHCO and VEH band structure calculations (eV).

Structure	Energy/Unit Cell[a]	Ionization Potential[b,c]	Bandgap[b]	Band Widths[b,d]
1a	−317.843	4.33	0.68	3.24, 3.59
1b	−635.217 (−317.609)[e]	4.03	0.00	2.77, 0.03 0.05, 3.29
1c	−317.646	4.06[f]	0.00	0.08, 7.21

[a]From EHCO calculations. [b]From VEH calculations. [c]1.9 eV subtracted from calculated values.[22] [d]For the highest occupied and lowest unoccupied bands in **1a**, the two highest occupied and two lowest unoccupied bands in **1b**, and the two half-occupied bands in **1c**. [e]Since the unit cell in **1b** is twice that in **1a** and **1c**, the energy per unit cell has to be divided by two (giving the value in parentheses) for comparison with the other structures. [f]Taken to be the crossing point of the two half-occupied bands.

crossing is moved from k=π/2a to the zone edge (k=π/a), because of the larger unit cell. Instead of an avoided crossing, the wide band splits into two bands, with a gap at the zone edge. The narrow band remains nearly completely degenerate. In all three cases, there is a very narrow band at the Fermi level. This, of course, produces a very high density of states at this level.[24] Formally, **1b** and **1c** are true metals, while **1a** has a small band gap and a low ionization potential compared to other conducting polymers. While one might expect that the parent polycyclobutadiene would be a very reactive substance, suitably substituted derivatives could have truly remarkable properties.

Conclusions

Unlike the analogous polyphenyls, which are essentially chains of benzene rings, the homologous structures based on cyclobutadiene exhibit structural and electronic properties quite unlike the monomer. Bi(cyclobutadienyl) is best considered as two allyls plus ethylene, tri(cyclobutadienyl) as two allyls plus dimethylenecyclobutanediyl,[28] and tetra(cyclobutadienyl) as two bi(cyclobutadienyl) units. The band structure of the infinite polymer is quite intriguing, suggesting a very small (or zero) band gap, and a high density of states near the Fermi level.

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Appendix: Z-matrices

Complete geometry specifications of the structures described in this chapter are given on the following pages in the form of Z-matrices.

2a:

1	C						
2	C	1	1.310432				
3	C	2	1.511264	1	136.953		
4	X	2	2.000000	1	90.000	3	0.000
5	C	2	2.081629	4	90.000	1	180.000
6	C	2	1.511264	1	136.953	3	180.000
7	C	1	1.511264	2	136.953	3	180.000
8	X	1	2.000000	2	90.000	6	0.000
9	C	1	2.081629	8	90.000	2	180.000
10	C	1	1.511264	2	136.953	3	0.000
11	X	3	2.000000	2	136.953	1	180.000
12	H	3	1.080634	11	88.782	2	180.000
13	X	5	2.000000	2	90.000	3	0.000
14	H	5	1.081395	13	90.000	2	180.000
15	X	6	2.000000	2	136.953	1	180.000
16	H	6	1.080634	15	88.782	2	180.000
17	X	7	2.000000	1	136.953	2	180.000
18	H	7	1.080634	17	88.782	1	180.000
19	X	9	2.000000	1	90.000	7	0.000
20	H	9	1.081395	19	90.000	1	180.000
21	X	10	2.000000	1	136.953	2	180.000
22	H	10	1.080634	21	88.782	1	180.000

2b:

1	C						
2	C	1	1.313310				
3	C	2	1.503169	1	137.986		
4	X	2	2.000000	1	90.000	3	0.000
5	C	2	2.067416	4	88.240	1	180.000
6	C	2	1.504202	1	136.203	3	180.000
7	C	1	1.503169	2	137.986	3	180.000
8	X	1	2.000000	2	90.000	6	0.000
9	C	1	2.067416	8	88.240	2	180.000
10	C	1	1.504202	2	136.203	3	0.000
11	X	3	2.000000	2	137.986	1	180.000
12	H	3	1.090000	11	90.000	2	180.000
13	X	5	2.000000	2	90.000	3	0.000
14	H	5	1.090000	13	90.000	2	180.000
15	X	6	2.000000	2	136.203	1	180.000
16	H	6	1.090000	15	90.000	2	180.000
17	X	7	2.000000	1	137.986	2	180.000
18	H	7	1.090000	17	90.000	1	180.000
19	X	9	2.000000	1	90.000	7	0.000
20	H	9	1.090000	19	90.000	1	180.000
21	X	10	2.000000	1	136.203	2	180.000
22	H	10	1.090000	21	90.000	1	180.000

2c:

1	C						
2	C	1	1.567124				
3	C	2	1.319573	1	90.000		
4	C	3	1.567124	2	90.000	1	0.000
5	C	3	1.455179	2	135.000	1	180.000
6	C	5	1.567124	3	135.000	2	0.000
7	C	6	1.319573	5	90.000	3	180.000
8	C	7	1.567124	6	90.000	5	0.000
9	H	1	1.090000	4	135.000	3	180.000

10	H	2	1.090000	1	135.000	4	180.000
11	H	4	1.090000	3	135.000	2	180.000
12	H	6	1.090000	5	135.000	8	180.000
13	H	7	1.090000	6	135.000	5	180.000
14	H	8	1.090000	7	135.000	6	180.000

2d:

1	C						
2	C	1	1.480000				
3	C	2	1.511264	1	136.953		
4	X	2	2.000000	1	90.000	3	0.000
5	C	2	2.081629	4	90.000	1	180.000
6	C	2	1.511264	1	136.953	3	180.000
7	C	1	1.511264	2	136.953	3	90.000
8	X	1	2.000000	2	90.000	6	-90.000
9	C	1	2.081629	8	90.000	2	180.000
10	C	1	1.511264	2	136.953	3	-90.000
11	X	3	2.000000	2	136.953	1	180.000
12	H	3	1.080634	11	90.000	2	180.000
13	X	5	2.000000	2	90.000	3	0.000
14	H	5	1.081395	13	90.000	2	180.000
15	X	6	2.000000	2	136.953	1	180.000
16	H	6	1.080634	15	90.000	2	180.000
17	X	7	2.000000	1	136.953	2	180.000
18	H	7	1.080634	17	88.782	1	180.000
19	X	9	2.000000	1	90.000	7	0.000
20	H	9	1.081395	19	90.000	1	180.000
21	X	10	2.000000	1	136.953	2	180.000
22	H	10	1.080634	21	90.000	1	180.000

2e:

1	C						
2	C	1	1.480000				
3	C	2	1.369000	1	135.000		
4	C	3	1.539000	2	90.000	1	180.000
5	C	4	1.369000	3	90.000	2	0.000
6	C	1	1.369000	2	135.000	3	90.000
7	C	6	1.539000	1	90.000	2	180.000
8	C	7	1.369000	6	90.000	1	0.000
9	H	3	1.090000	2	135.000	1	0.000
10	H	4	1.090000	3	135.000	2	180.000
11	H	5	1.090000	4	135.000	3	180.000
12	H	6	1.090000	1	135.000	2	0.000
13	H	7	1.090000	6	135.000	1	180.000
14	H	8	1.090000	7	135.000	6	180.000

2f:

1	C						
2	C	1	1.33094				
3	C	2	1.49518	1	136.734		
4	X	2	2.00000	1	90.000	3	0.000
5	C	2	2.07828	4	90.000	1	180.000
6	C	2	1.49518	1	136.734	3	180.000
7	C	1	1.49518	2	136.734	3	180.000
8	X	1	2.00000	2	90.000	6	0.000
9	C	1	2.07828	8	90.000	2	180.000
10	C	1	1.49518	2	136.734	3	0.000
11	X	3	2.00000	2	136.734	1	180.000

12	H	3	1.09000	11	90.000	2	180.000
13	X	5	2.00000	2	90.000	3	0.000
14	H	5	1.09000	13	90.000	2	180.000
15	X	6	2.00000	2	136.734	1	180.000
16	H	6	1.09000	15	90.000	2	180.000
17	X	7	2.00000	1	136.734	2	180.000
18	H	7	1.09000	17	90.000	2	180.000
19	X	9	2.00000	1	90.000	7	0.000
20	H	9	1.09000	19	90.000	1	180.000
21	X	10	2.00000	1	136.734	2	180.000
22	H	10	1.09000	21	90.000	1	180.000

2g:

1	C						
2	C	1	1.33227				
3	C	2	1.49318	1	137.724		
4	X	2	2.00000	1	90.000	3	0.000
5	C	2	2.07525	4	90.574	1	180.000
6	C	2	1.49354	1	136.568	3	180.000
7	C	1	1.49318	2	137.724	3	180.000
8	X	1	2.00000	2	90.000	6	0.000
9	C	1	2.07525	8	90.574	2	180.000
10	C	1	1.49394	2	136.568	3	0.000
11	X	3	2.00000	2	137.724	1	180.000
12	H	3	1.09000	11	90.000	2	180.000
13	X	5	2.00000	2	90.000	3	0.000
14	H	5	1.09000	13	90.000	2	180.000
15	X	6	2.00000	2	136.568	1	180.000
16	H	6	1.09000	15	90.000	2	180.000
17	X	7	2.00000	1	136.724	2	180.000
18	H	7	1.09000	17	90.000	2	180.000
19	X	9	2.00000	1	90.000	7	0.000
20	H	9	1.09000	19	90.000	1	180.000
21	X	10	2.00000	1	136.568	2	180.000
22	H	10	1.09000	21	90.000	1	180.000

3a:

1	C						
2	X	1	1.04779				
3	C	2	1.02735	1	90.000		
4	C	2	1.04779	3	90.000	1	180.000
5	C	2	1.02735	4	90.000	3	180.000
6	C	2	2.41059	3	90.000	1	0.000
7	C	2	2.41059	5	90.000	4	0.000
8	C	6	1.49676	1	136.756	3	180.000
9	C	7	1.49676	4	136.756	5	180.000
10	C	2	4.48035	3	90.000	1	0.000
11	C	2	4.48035	5	90.000	4	0.000
12	C	6	1.49676	1	136.756	3	0.000
13	C	7	1.49676	4	136.756	5	0.000
14	H	2	2.09771	1	90.000	3	0.000
15	H	2	2.09771	4	90.000	5	0.000
16	H	8	1.07064	6	133.327	1	0.000
17	H	9	1.07064	7	133.327	4	0.000
18	H	12	1.07064	6	133.327	1	0.000
19	H	13	1.07064	7	133.327	4	0.000
20	H	2	5.55510	3	90.000	1	0.000
21	H	2	5.55510	5	90.000	4	0.000

3b:

1	X						
2	C	1	1.00000				
3	C	2	1.36772	1	47.855		
4	C	2	2.06958	3	47.855	1	0.000
5	C	4	1.36772	2	47.855	3	180.000
6	C	2	1.41730	3	138.054	4	180.000
7	C	4	1.41730	5	138.054	2	180.000
8	C	6	1.36834	2	138.054	3	180.000
9	C	7	1.36834	4	138.054	5	180.000
10	C	8	1.52495	6	90.570	2	180.000
11	C	9	1.52495	7	90.570	4	180.000
12	C	6	1.54382	2	132.642	3	0.000
13	C	7	1.54382	4	132.642	5	0.000
14	H	3	1.07210	2	137.530	5	180.000
15	H	5	1.07210	4	137.530	3	180.000
16	H	8	1.07201	6	131.627	2	0.000
17	H	9	1.07201	7	131.627	4	0.000
18	H	12	1.07157	6	131.905	2	0.000
19	H	13	1.07157	7	131.905	4	0.000
20	H	10	1.07169	8	90.000	6	180.000
21	H	11	1.07169	9	90.000	7	180.000

4a:

1	C						
2	C	1	1.43482				
3	C	2	1.42585	1	134.152		
4	C	1	1.42585	2	134.152	3	0.000
5	C	2	1.42585	1	134.152	4	180.000
6	C	1	1.42585	2	134.152	3	180.000
7	X	2	1.00000	1	90.000	4	0.000
8	C	2	2.08017	7	90.000	1	180.000
9	X	1	1.00000	2	90.000	3	0.000
10	C	1	2.08017	9	90.000	2	180.000
11	C	2	3.42979	7	90.000	1	180.000
12	C	1	3.42979	9	90.000	2	180.000
13	C	11	1.48405	8	136.261	3	0.000
14	C	12	1.48405	10	136.261	4	0.000
15	C	11	1.48405	8	136.261	3	180.000
16	C	12	1.48405	10	136.261	4	180.000
17	C	2	5.50484	7	90.000	1	180.000
18	C	1	5.50484	9	90.000	2	180.000
19	H	3	1.07104	2	135.875	1	0.000
20	H	4	1.07104	1	135.875	2	0.000
21	H	5	1.07104	2	135.875	1	0.000
22	H	6	1.07104	1	135.875	2	0.000
23	H	13	1.07065	11	133.773	8	0.000
24	H	14	1.07065	12	133.773	10	0.000
25	H	15	1.07065	11	133.773	8	0.000
26	H	16	1.07065	12	133.773	10	0.000
27	H	2	6.57733	7	90.000	1	180.000
28	H	1	6.57733	9	90.000	2	180.000

4b:

1	C						
2	C	1	1.43482				
3	C	2	1.42585	1	134.152		
4	C	1	1.42585	2	134.152	3	90.000
5	C	2	1.42585	1	134.152	3	180.000
6	C	1	1.42585	2	134.152	4	180.000
7	X	2	1.00000	1	90.000	3	0.000
8	C	2	2.08017	7	90.000	1	180.000
9	X	1	1.00000	2	90.000	4	0.000
10	C	1	2.08017	9	90.000	2	180.000
11	C	2	3.42979	7	90.000	1	180.000
12	C	1	3.42979	9	90.000	2	180.000
13	C	11	1.48405	8	136.261	3	0.000
14	C	12	1.48405	10	136.261	4	0.000
15	C	11	1.48405	8	136.261	3	180.000
16	C	12	1.48405	10	136.261	4	180.000
17	C	2	5.50484	7	90.000	1	180.000
18	C	1	5.50484	9	90.000	2	180.000
19	H	3	1.07104	2	135.875	1	0.000
20	H	4	1.07104	1	135.875	2	0.000
21	H	5	1.07104	2	135.875	1	0.000
22	H	6	1.07104	1	135.875	2	0.000
23	H	13	1.07065	11	133.773	8	0.000
24	H	14	1.07065	12	133.773	10	0.000

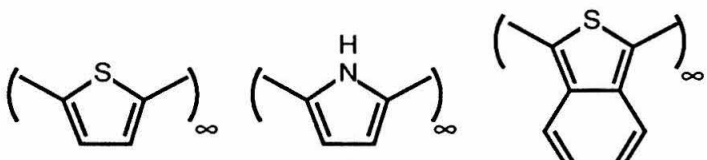
25	H	15	1.07065	11	133.773	8	0.000
26	H	16	1.07065	12	133.773	10	0.000
27	H	2	6.57733	7	90.000	1	180.000
28	H	1	6.57733	9	90.000	2	180.000

Chapter 4

Orbital Interactions in Conjugated Polymers: The Band Structures of Polyfulvene and Related Polymers

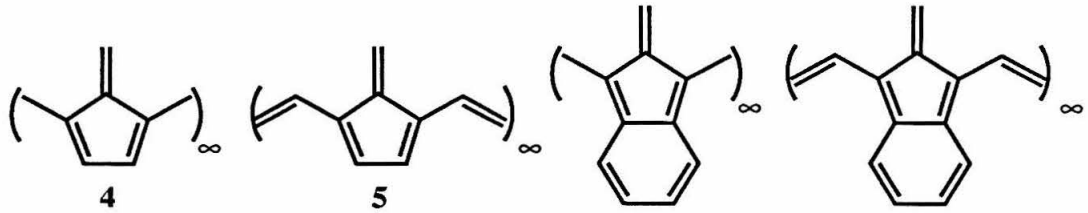
The study of electrically conducting organic polymers is currently an active field of research in both experimental and theoretical chemistry.[1] Interest in this field originated with the discovery by Shirakawa and co-workers that films of polyacetylene could be "doped" with electron donors or acceptors to form materials whose electrical conductivities approach those of some metals.[2] Since this initial discovery, a variety of electrically conducting polymers have been synthesized and studied both experimentally and theoretically.

Among the most studied of these compounds are those based on five-membered aromatic rings, such as polythiophene (**1**),[3] polypyrrole (**2**),[4] and related structures. Recently the benzannelated derivative polyisothianaphthene (**3**) has been prepared and found to have quite intriguing and potentially useful properties,[5] including the fact that it appears to be a transparent conductor. These findings have been supplemented by theoretical work on such ring systems.[6–8]



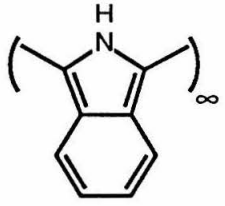
1 **2** **3**

Polyfulvene (**4**) is a nonaromatic hydrocarbon analogue of polypyrrole and polythiophene. It may also be viewed as a nonalternant isomer of polyphenylene. In this chapter we present the results of theoretical studies of some polymers based on the fulvene system, in order to assess their viability as conducting polymers. The systems we studied include polyfulvene-vinylene (**5**), polyisobenzofulvene (**6**), and poly-isobenzofulvene-vinylene (**7**), as well as polyfulvene itself. The latter two are, of course, analogues of polyisothianaphthene.



4 5 6 7

In the course of this work we have developed a new model for the effects of benzannelation, and we have applied this model to polyisothianaphthene and the nitrogen analogue polyisobenzopyrrole (**8**). After this work was completed, we became aware of several papers by Kertesz and Lee that include a similar analysis on **1** and **3**.[8]



8

Electronic Structure of Polymers

Calculation of Band Structures.[9] The polymers we consider in this chapter are infinite systems characterized by the presence of one axis of translational symmetry. In other words, the system consists of an infinite one-dimensional array of identical "unit cells". Each unit cell contains one or several atoms.

As with finite molecular systems, most theoretical calculations on polymers are based on the linear combination of atomic orbitals (LCAO) formalism. The problem is that with an infinite system, one has to deal with a basis set consisting of an infinite number of atomic orbitals. This problem can be overcome by utilizing the translational symmetry of the system. Suppose there are 2N+1 unit cells, labelled from –N to N, and n atomic orbitals within each unit cell. The atomic orbitals that are equivalent under the translational symmetry can be combined to form the Bloch orbitals,

$$\Phi_\mu(k) = (2N+1)^{-1/2} \sum_{j=-N}^{N} e^{ikaj} \chi^j_\mu \qquad \mu=1,2,\ldots,n, \tag{1}$$

where χ^j_μ is the μth atomic orbital in the jth unit cell, a is the length of the unit cell, and k is an index with a value anywhere between $-\pi/a$ and π/a. (This range of k values is called the first Brillouin zone, in the terminology of solid-state physics.) The Bloch orbitals $\Phi_\mu(k)$ are simply symmetry-adapted linear combinations of the atomic orbitals χ^j_μ.

The molecular orbitals (or "crystal orbitals" in solid-state terminology) are then obtained as linear combinations of these Bloch orbitals,

$$\phi_i(k) = \sum_{\mu=1}^{n} C_{i\mu}(k)\Phi_\mu(k) \qquad i=1,2,\ldots,n. \tag{2}$$

The coefficients $C_{i\mu}(k)$ are found as the eigenvectors and the corresponding orbital energies $E_i(k)$ as the eigenvalues of the equation

$$\sum_\mu F_{\mu\nu}(k)C_{i\mu}(k) = E_i(k)\sum_\mu S_{\mu\nu}(k)C_{i\mu}(k), \tag{3}$$

where $F_{\mu\nu}(k)$ is a Fock matrix element between Bloch orbitals,

$$F_{\mu\nu}(k) = \langle \Phi_\mu(k) | \hat{F} | \Phi_\nu(k) \rangle, \tag{4}$$

and $S_{\mu\nu}(k)$ is an overlap matrix element, also between Bloch orbitals,

$$S_{\mu\nu}(k) = \langle \Phi_\mu(k) | \Phi_\nu(k) \rangle. \tag{5}$$

From the definition of Bloch orbitals (eq.1), these can be expressed in terms of the atomic orbitals

$$F_{\mu\nu}(k) = \sum_{j=-N}^{N} e^{ikaj} F^j_{\mu\nu}, \tag{6}$$

$$S_{\mu\nu}(k) = \sum_{j=-N}^{N} e^{ikaj} S^j_{\mu\nu}, \tag{7}$$

where $F^j_{\mu\nu}$ and $S^j_{\mu\nu}$ are the Fock and overlap matrix elements between the atomic orbital χ^0_μ in a given unit cell (the "origin" unit cell) and χ^j_ν in the jth neighboring unit cell

$$F^j_{\mu\nu} = \langle \chi^0_\mu | \hat{F} | \chi^j_\nu \rangle, \tag{8}$$

$$S^j_{\mu\nu} = \langle \chi^0_\mu | \chi^j_\nu \rangle. \tag{9}$$

In actual calculations, of course, it is necessary to truncate the infinite summations in Eqs. 6 and 7.

The algorithm for calculating polymer band structure is thus as follows: (1) the Fock and overlap matrix elements between various atomic orbitals in various unit cells are calculated (Eqs. 8 and 9); (2) these are summed, for a given value of k, to obtain matrix elements between Bloch orbitals (Eqs. 6 and 7); (3) Equation 3 is then solved to give the eigenvalues (orbital energies) and eigenvectors (crystal orbital coefficients) for that value of k; (4) steps 2 and 3 are repeated for various values of k between 0 and $\pi/2$. (It is not necessary to do the calculation for $-\pi/2 \leq k < 0$, because the solution for k=x is the same as for k=−x; this is obvious from the form of Eqs. 6, 7, and 1.)

The actual calculation of matrix elements between atomic orbitals (step 1, Eqs. 8 and 9) depends on the method used. In this work we have used simple Hückel molecular orbital theory (HMO),[10] the extended Hückel crystal orbital method (EHCO; this is just ordinary extended Hückel theory applied to polymer systems)[11], and the valence effective hamiltonian method (VEH).[12]

HMO.[10] The well-known approximations of Hückel theory are: (1) only orbitals of π symmetry are considered; (2) the atomic orbitals that form the basis set are orthonormal; thus, the overlap matrix is a unit matrix; (3) two-electron integrals are ignored; (4) the energy of each atomic orbital prior to interaction is equal to α; (5) the interaction energy between two atomic orbitals that are nearest neighbors is equal to β; (6) the interaction energy between two atomic orbitals that are not nearest neighbors is zero.

Thus, in HMO theory, the Fock matrix elements are given by

$$F_{\mu\nu} = \begin{cases} \alpha & \mu = \nu \\ \beta & \mu \neq \nu, \text{ nearest neighbors} \\ 0 & \mu \neq \nu, \text{ nonnearest neighbors,} \end{cases} \tag{10}$$

and the overlap matrix elements by

$$S_{\mu\nu} = \begin{cases} 1 & \mu = \nu \\ 0 & \mu \neq \nu \end{cases} \tag{11}$$

EHCO.[11] Extended Hückel theory is a straightforward extension of simple Hückel theory.[13] Its features are: (1) Valence orbitals of σ as well as π symmetry are explicitly considered, but not core orbitals (thus, carbon 1s orbitals, for example, are ignored); (2) the overlap matrix elements are calculated explicitly, with each atomic orbital represented by a Slater orbital with the appropriate exponent ζ; (3) two-electron integrals are ignored; (4) the diagonal elements of the Fock matrix (i.e., the energy of the atomic orbitals prior to interaction) are taken to be equal to the valence state ionization potential of that particular orbital; (5) in the original formulation, the off-diagonal Fock matrix elements are approximated by the Wolfsberg–Helmholtz formula[13]

$$F_{\mu\nu} = \frac{KS_{\mu\nu}}{2}(F_{\mu\mu}+F_{\nu\nu}), \tag{12}$$

where K is usually taken to be 1.75. This formulation has now been superseded by a modified formula[14]

$$F_{\mu\nu} = \frac{[K-(K-1)\Delta^2]S_{\mu\nu}}{2}\left[(1+\Delta)F_{\mu\mu}+(1-\Delta)F_{\nu\nu}\right], \tag{13}$$

where

$$\Delta = \frac{F_{\mu\mu}-F_{\nu\nu}}{F_{\mu\mu}+F_{\nu\nu}}. \tag{14}$$

In an extended Hückel calculation, the total energy of a molecule is simply twice the sum of the energies of the occupied orbitals (assuming the molecule to be a closed-shell system, with no singly occupied orbitals).[13] For polymers, the sum over occupied

molecular orbitals is replaced by an integral over occupied crystal orbitals, since the latter is a continuous function of energy.[11]

Parameters for an extended Hückel calculation are the Slater orbital exponents (ζ_μ) and the valence state ionization potential ($F_{\mu\mu}$) for each atomic orbital. These are shown in Table I.

VEH.[12] The VEH method is similar to the extended Hückel method in that a Fock matrix is constructed and diagonalized once without any iterative SCF process. In this method, the Fock operator is assumed to have the form

$$\hat{F} = \hat{T} + \sum_A \hat{V}_A, \tag{15}$$

where $\hat{T}$ is the kinetic energy operator and $\hat{V}_A$ is the "effective potential" of atom A; the summation is over all the atoms in the system. The effective potentials are assumed to have the form

$$\hat{V}_A = \sum_{l,m,i,j} C^A{}_{ijlm} |\xi^A{}_{ilm}\rangle\langle\xi^A{}_{jlm}|. \tag{16}$$

The summations over l and m define the angular dependence of $\hat{V}_A$. Each ξ_{ilm} is a normalized gaussian function

$$\xi_{ilm} = N_i \exp(-\alpha_i r^2) Y_{lm}(\theta,\varphi), \tag{17}$$

where N_i is a normalization factor and $Y_{lm}(\theta,\varphi)$ indicates the usual spherical harmonics. Only 1s and 2p gaussian cartesian functions are used. Note that the ξ_{ilm}s are *not* supposed to represent atomic orbitals, although their functional forms are like those of AOs.

Overlap matrix elements are calculated explicitly, using the STO-3G basis set[15] for the atomic orbitals, except that only the valence orbitals are considered. The Fock matrix elements are calculated using equation 15; i.e.,

$$F_{\mu\nu} = \langle\chi_\mu|\hat{T}|\chi_\mu\rangle + \sum_{A,l,m,i,j} C^A{}_{ijlm} \langle\chi_\mu|\xi^A{}_{ilm}\rangle\langle\xi^A{}_{jlm}|\chi_\nu\rangle. \tag{18}$$

Table I. Extended Hückel parameters.[a]

χ_μ	ζ_μ	$F_{\mu\mu}$ (eV)
H 1s	1.3	−13.6
C 2s	1.625	−21.4
C 2p	1.625	−11.4
S 3s	1.817	−20.0
S 3p	1.817	−13.3
N 2s	1.950	−26.0
N 2p	1.950	−13.4
O 2s	2.275	−32.3
O 2p	2.275	−14.8

[a]Heteroatom parameters included for completeness. For the work presented in this chapter, we did not perform EHCO calculations on polymers containing heteroatoms.

The kinetic energy terms are calculated explicitly (recall that $\hat{T}$ is simply $-\nabla^2/2$ when expressed in atomic units). In principle, the summation over A needs to be carried out over all the atoms in the system; in practice, the summation converges quite rapidly because of the exponential decrease of the overlap-like terms, and only atoms in the origin unit cell and a few neighboring unit cells need to be considered.

VEH parameters suitable for polymer calculations have been derived by Brédas and co-workers.[12b–12e] These are shown in Table II. They are optimized to reproduce the energies of occupied molecular orbitals obtained by ab initio calculations using a double zeta basis set. Thus, energies of unoccupied orbitals obtained by a VEH calculation are often unreliable. Indeed, when applied to polymers, the VEH method often predicts spuriously low-lying σ^* bands. However, the lowest lying π^* band is calculated correctly, allowing the calculation of π band gaps.

Interpretation of Polymer Band Structures.[10] The term "band structure" is generally used to mean a plot of the crystal orbital energies as a function of k. This is usually given for $0 \leq k \leq \pi/a$, i.e., for half of the first Brillouin zone. As an example, the VEH π-band structure of polyacetylene is shown in Figure 1, which also defines the terminology used in discussing band structures. Each band may be thought of as arising from one molecular orbital of the fragment that forms the unit cell. In Figure 1, the two MOs are the π and π^* orbitals of ethylene.

Each value of k corresponds to a particular phase relationship between the MOs in adjacent unit cells. At k=0 (the Brillouin zone center), the MOs in adjacent unit cells are fully in phase; at $k=\pi/a$ (the zone edge), they are fully out of phase. This phase relationship explains the existence of a band gap in polyacetylene. At the Fermi level (the top of the valence band), there are bonding (intracell) interactions between doubly bonded atoms, and antibonding (intercell) interactions between singly bonded atoms. At the bottom of the conduction band, the bonding interactions are between singly bonded

Table II. VEH parameters.

Atom	l	m	i	j	α_i	C_{ijlm}
C	0	0	1	1	3.63	−10.075
			2	2	0.33	−1.178
			1	2		2.077
	1	−1,0,+1	1	1	6.50	−11.468
			2	2	0.52	−0.443
			1	2		−0.185
H	0	0	1	1	5.00	−4.696
			2	2	0.49	−0.500
			1	2		0.646
S	0	0	1	1	1.00	3.683
			2	2	0.30	1.521
			1	2		−3.454
	1	−1,0,+1	1	1	0.90	−1.899
			2	2	0.20	−0.047
			1	2		−0.017
C(-S)[a]	0	0	1	1	3.63	−6.506
			2	2	0.33	−0.514
			1	2		0.354
	1	−1,0,+1	1	1	6.50	−12.380
			2	2	0.52	−0.514
			1	2		0.354
N	0	0	1	1	1.50	1.520
			2	2	0.50	0.790
			1	2		−2.149
	1	−1,0,+1	1	1	3.00	−4.789
			2	2	0.35	0.046
			1	2		−0.353

Table II. (continued)

Atom	l	m	i	j	α_i	C_{ijlm}
C(-N)[b]	0	0	1	1	3.63	–0.486
			2	2	0.33	0.222
			1	2		–1.710
	1	–1,0,+1	1	1	6.50	–1.637
			2	2	0.52	0.244
			1	2		–2.834
O[d]	0	0	1	1	5.00	–8.559
			2	2	0.50	–1.387
			1	2		1.107
	1	–1,0,+1	1	1	2.89	–5.364
			2	2	0.065	–0.065
			1	2		–0.045
C(-O)[c,d]	0	0	1	1	3.63	–5.347
			2	2	0.33	–0.224
			1	2		–0.212
	1	–1,0,+1	1	1	6.50	–4.315
			2	2	0.52	0.063
			1	2		–2.192

[a]Carbon bonded to sulfur. [b]Carbon bonded to nitrogen. [c]Carbon bonded to oxygen. [d]Parameters for oxygen are listed for the sake of completeness; none of the polymers discussed in this chapter contains oxygens.

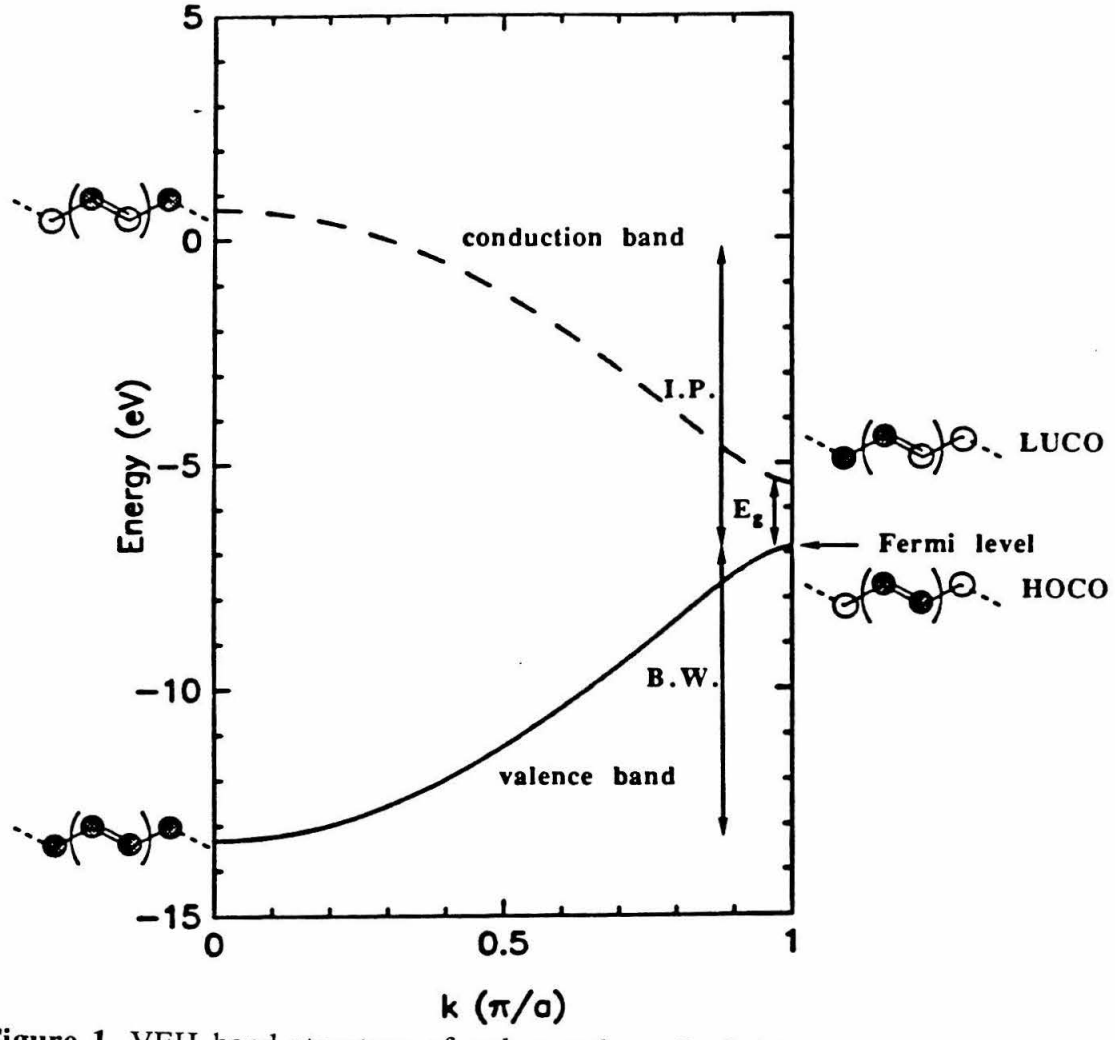


Figure 1. VEH band structure of polyacetylene. Definitions of the terms used in discussing conducting polymers are shown.

atoms, and the antibonding interactions between doubly bonded atoms. Thus, the HOCO (highest occupied crystal orbital) has a lower energy than the LUCO (lowest unoccupied crystal orbital). If all the bond lengths were the same, the HOCO will have the same energy as the LUCO, and a zero band gap (indicative of a metallic state) will result. The distortion from all-equal bonds to alternating single and double bonds in polyacetylene is an example of a Peierls distortion, the solid-state term for a Jahn–Teller distortion.

In the context of conducting polymers, three parameters of interest are the ionization potential (IP), band gaps (E_g), and band widths (BW) (Figure 1). The ionization potential is a measure of the ease of oxidation of the material, which is important when doping with electron acceptors is desired. The band gap identifies the nature of the material: a large band gap is indicative of an insulator; a small band gap, a semiconductor; and a zero band gap, a metal. The ionization potential minus the band gap gives the electron affinity of the system, which is a measure of the ease of reduction of the material. Finally, the band width is a measure of the mobility of electrons along the polymer chain. A large band width indicates large intercell interactions, hence good electron mobility. For conducting polymers, one desires a small IP, a small (or zero) E_g, and a large BW.

Computational Methods

In this work we have used the HMO,[10] EHCO,[11] and VEH[12] methods to perform band structure calculations on **1**–**8**. HMO was used as an exploratory tool to map out the qualitative features of the band structures. EHCO and VEH were used for more quantative calculations. We have used EHCO primarily to calculate energy differences between alternative structures (fulvenoid and quinoid; see below). IPs, E_gs, and BWs are calculated using the more accurate VEH method.[16]

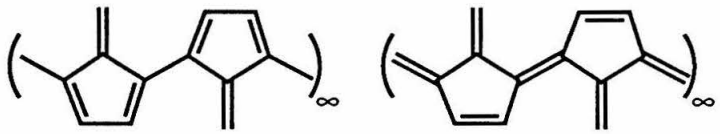
HMO and VEH calculations were performed with the programs listed in Appendix B. The EHCO program was kindly provided by Professor Myung-Hwan Whangbo. In the EHCO calculations, interactions up to the second neighboring unit cell are included in Eqs. 6 and 7; in the VEH calculations, interactions up to the fourth neighboring unit cell are included.

All the band structure calculations assumed a planar structure. In **4** and **6**, steric interactions will almost certainly lead to nonplanar structures. In fact, an MNDO calculation on fulvene dimer predicts essentially orthogonal rings. Thus, we do not expect the band structures we obtain for these materials to be accurate representations of the true polymers. We have included them primarily for the purpose of analysis. However, these steric interactions are greatly diminished when vinylene groups are used to space out the rings, as in **5** and **7**. For example, CPK models, which if anything tend to overestimate steric repulsions, clearly show that a planar structure is feasible for **7**. We therefore expect these "vinylogues" to be essentially planar, and (as shown below) they are thus quite promising candidates for organic conductors. In addition, one can envision efficient synthetic routes to the vinylogues, using the ring-opening metathesis polymerization (ROMP) chemistry recently developed by Grubbs and co-workers.[17,18]

In order to preserve translational symmetry, the VEH and EHCO calculations employed a unit cell consisting ot two ring units, with the rings oriented alternately up and down. The band structures so obtained were then unfolded to obtain the band structure corresponding to monomeric unit cells. Thus the band structures shown in Figures 3 and 8 correspond to polymers that do *not* possess full translational symmetry; instead, they have a twofold screw-symmetry axis along the polymer chain. This necessitates an additional phase factor of π in formulating the Bloch orbitals (Eq. 1), causing the Brillouin zone to be "shifted" by π/a. Thus, the crystal orbitals consist of

fully in-phase combination of unit cell MOs at the zone *edge* (k=π/a) and fully out-of-phase combination at the zone *center* (k=0).[19]

For the polymers **3**–**7**, two geometries were considered. One corresponds to a fulvenoid geometry, with single bonds external to the rings, while the other corresponds to a "quinoid" geometry, with double bonds external to the rings. These are shown below for polyfulvene; analogous structures for the other polymers are easily visualized.



fulvenoid **quinoid**

For polypyrrole and polythiophene, of course, the analogue to the fulvenoid geometry is strongly preferred because it is aromatic. Fulvene, however, is not aromatic, and it is not clear whether the fulvenoid or quinoid form is the more stable. For the benzannelated compounds **6** and **7**, one might expect the quinoid form to be favored, since it allows a classically aromatic six-membered ring. This is precisely opposite to the situation in **3** and **8**.

The geometries used for VEH and EHCO calculations are shown in Figure 2. In most cases, they are based on MNDO-optimized geometries of the corresponding monomers.[20] The MNDO structure for fulvene agrees reasonably well with the experimental structure obtained from microwave spectra;[21] no experimental data are available for comparison to the other structures.

Results and Discussion

What initially intrigued us about polyfulvene was its HMO band structure, shown in Figure 3. There is an exact degeneracy between the valence and conduction bands, which occurs at the Fermi level. This is, of course, what is seen in polyacetylene when treated at a similar level.[10]

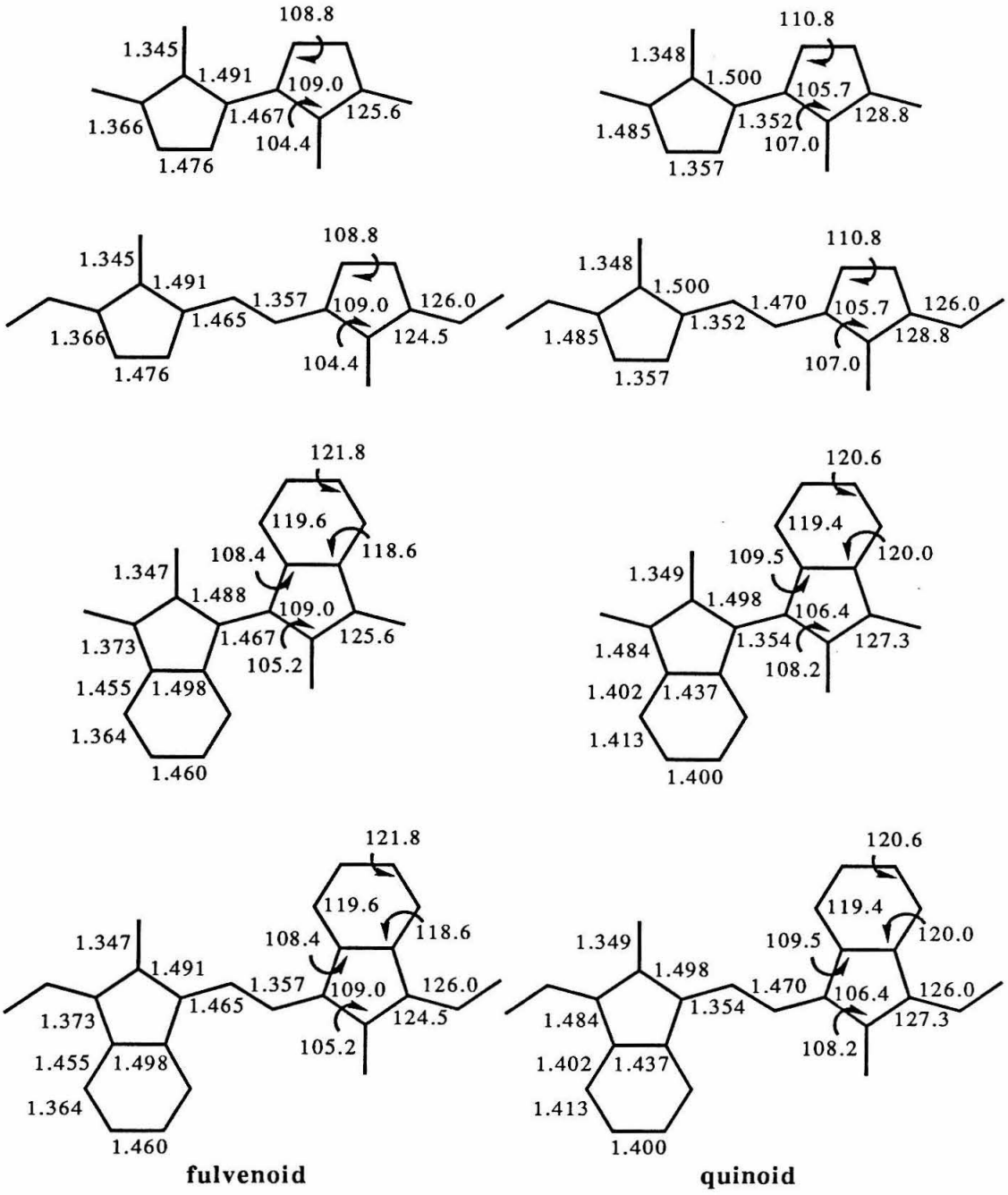


Figure 2. Geometries of **4**, **5**, **6**, and **7** used in the band structure calculations. Bond lengths in angstroms, angles in degrees.

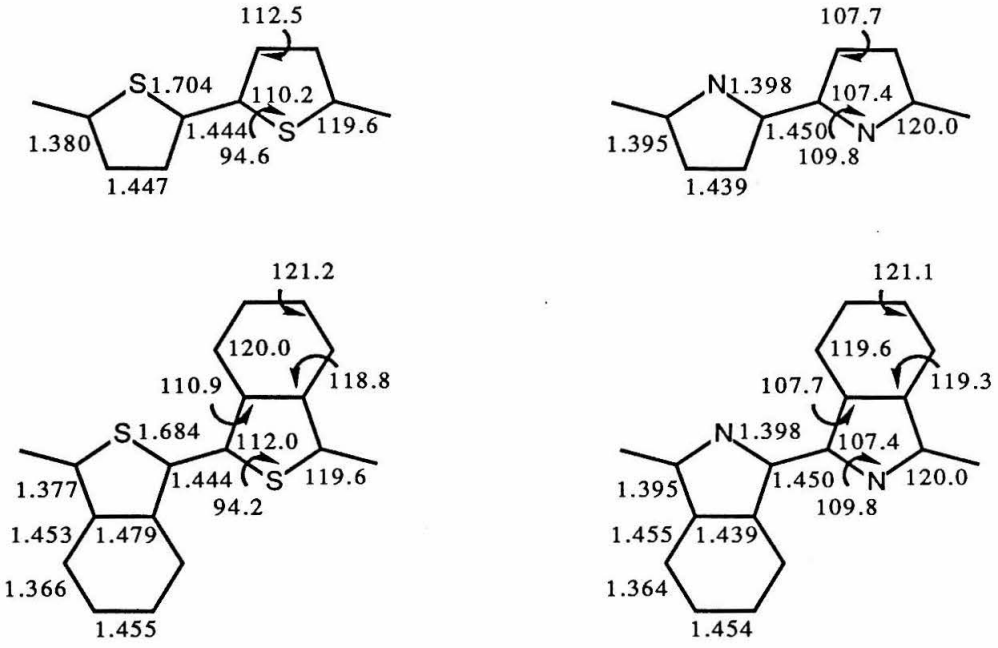


Figure 2 (continued). Geometries of **1**, **2**, **3**, and **8** used in the band structure calculations.

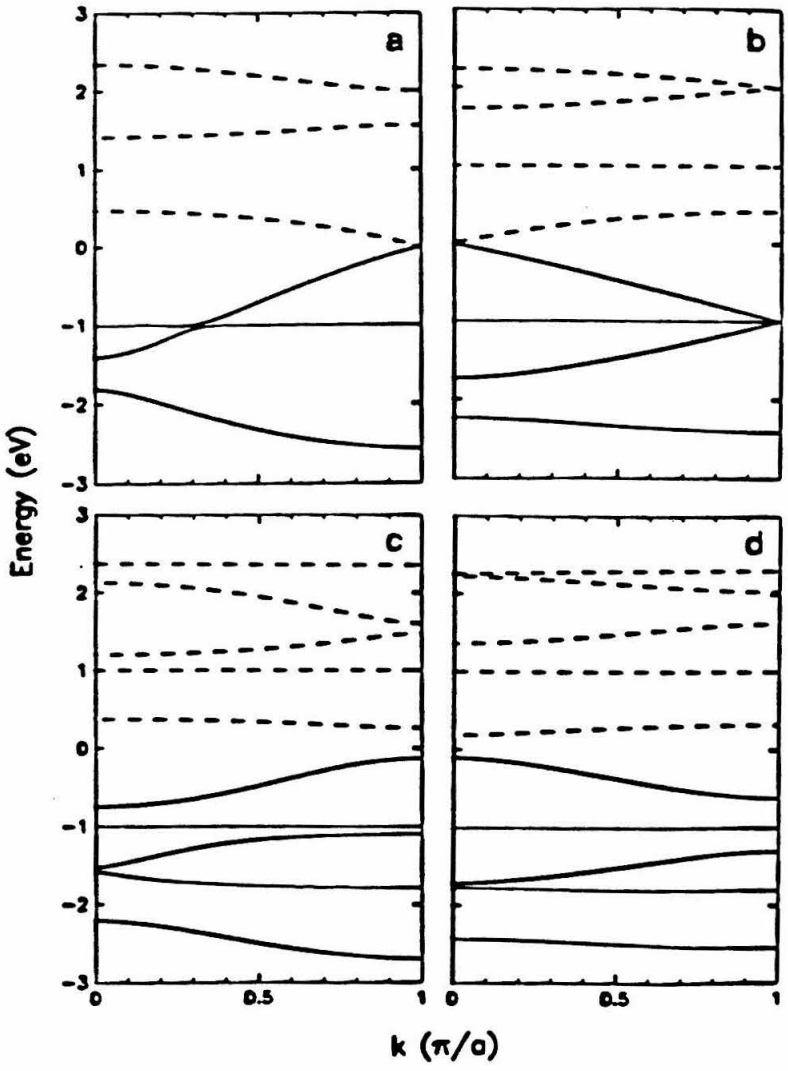


Figure 3. HMO band structures of (a) **4**, (b) **5**, (c) **6**, and (d) **7**. The zero of energy corresponds to the energy of an isolated *p* orbital (α). Solid lines indicate occupied bands; dashed lines indicate empty bands. In (d) the bands at E=β and E=$-\beta$ are doubly degenerate.

The origin of this effect can be understood after an examination of the HOMO and LUMO of fulvene (Figure 4). The HOMO is just the out-of-phase combination of the two π bonds of the ring. The LUMO is the in-phase combination of the π^* orbitals of these double bonds, plus a contribution from the exocyclic CH_2 and a small contribution from the ring carbon bonded to it. These two orbitals are, respectively, antisymmetric (A) and symmetric (S) with regard to a mirror plane that is perpendicular to the molecular plane and contains the exocyclic C–C bond. Inspection of the valence and conduction bands of **4** at the zone edge ($k=\pi/a$, where the degeneracy occurs), reveals their origin (Figure 5). The HOCO derives from the HOMO of fulvene, and is precisely analogous to the HOCO in polyacetylene. There are exactly as many in-phase nearest-neighbor interactions as there are out-of-phase interactions, so the orbital is net nonbonding ($E=\alpha$ in HMO). Similarly, the LUCO, derived from the LUMO of fulvene, has equal numbers of in-phase and out-of-phase interactions, plus a contribution from the exocyclic CH_2. However, unlike the LUMO of fulvene, the LUCO of the polymer at the HMO level has no contribution from the carbon bonded to the exocyclic CH_2. The CH_2 experiences no nearest-neighbor interactions in this orbital and so cannot make this orbital any more or less stable than an isolated *p* orbital.

In actual polyfulvene, two factors would operate to remove the HOCO/LUCO degeneracy. The first is a Peierls distortion analogous to that seen in polyacetylene. Bond alternation (in standard HMO all bonds are the same length) could be introduced in one of two ways, producing either the fulvenoid or quinoid structures. As pointed out above, it is not certain which structure is energetically favored. Consideration of nonnearest-neighbor interactions would also split the degeneracy. The VEH and EHCO calculations include both these effects. The results from HMO, however, are usually qualitatively correct. Interestingly, polythiophene and polypyrrole do not possess a comparable

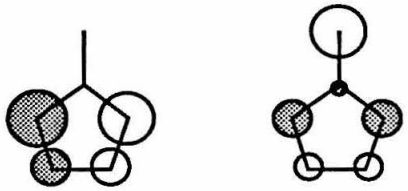


Figure 4. HOMO and LUMO of fulvene at the HMO level.

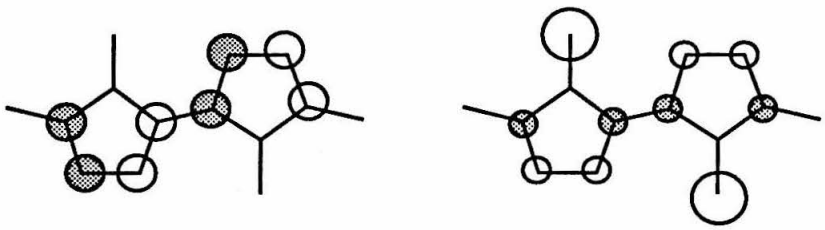


Figure 5. HOCO and LUCO of **4** at the HMO level.

HOCO/LUCO degeneracy in HMO. This suggests that **4** could have a smaller E_g than these known conducting polymers.

The HOCO/LUCO degeneracy persists in **5**, at the HMO level (Figure 3), and arguments exactly analogous to those for **4** explain this result (remembering that the degeneracy for **5** occurs at the zone center, k=0). The HOCO of **5** (Figure 7) arises from the HOMO of trimethylenecyclopentene (Figure 6), and the LUCO from the LUMO. In both COs, there are exactly as many in-phase and out-of-phase nearest-neighbor interactions, making them degenerate with $E=\alpha$. Note, however, that in this case the HOMO (and HOCO) is S, and the LUMO (and LUCO) is A.

Fusion of a benzene ring to produce the benzanellated polymers **6** and **7** removes the degeneracy, even at the HMO level (Figure 3).

The VEH band structures for **4**–**7** in both the fulvenoid and quinoid geometries are shown in Figure 8. Table III presents the IP, E_g, and BW data obtained from the band structures, as well as the total energies per unit cell obtained from EHCO calculations. For comparison, the VEH data for **1**–**3** and **8** are also shown in Table III. As predicted by HMO, E_g for polyfulvene *at the fulvenoid geometry* is much smaller than for polypyrrole and even polythiophene. We consider this to be a manifestation of the Hückel degeneracy.

Brédas and co-workers have investigated the effect of bond-length alternation on the electronic structure of polyphenylene, polypyrrole, and polythiophene.[7,22] They concluded that a substantial reduction in E_g can be obtained by increasing the quinoid character of the structures.[7] Given this conclusion, our results for the fulvene-based polymers are at first sight surprising. In all four cases the quinoid forms have the greater band gaps. An explanation can be found in a more detailed consideration of the HOCO and LUCO of these structures.

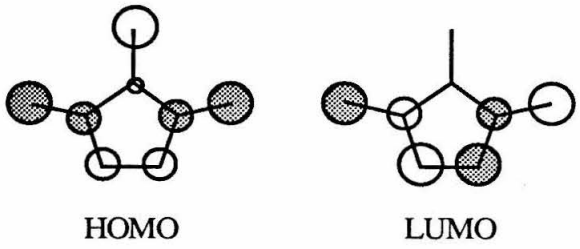


Figure 6. HOMO and LUMO of trimethylenecyclopentene at the HMO level.

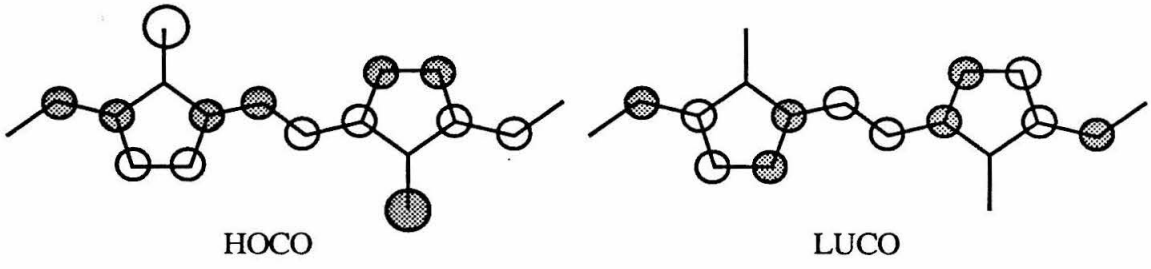


Figure 7. HOCO and LUCO of **5** at the HMO level.

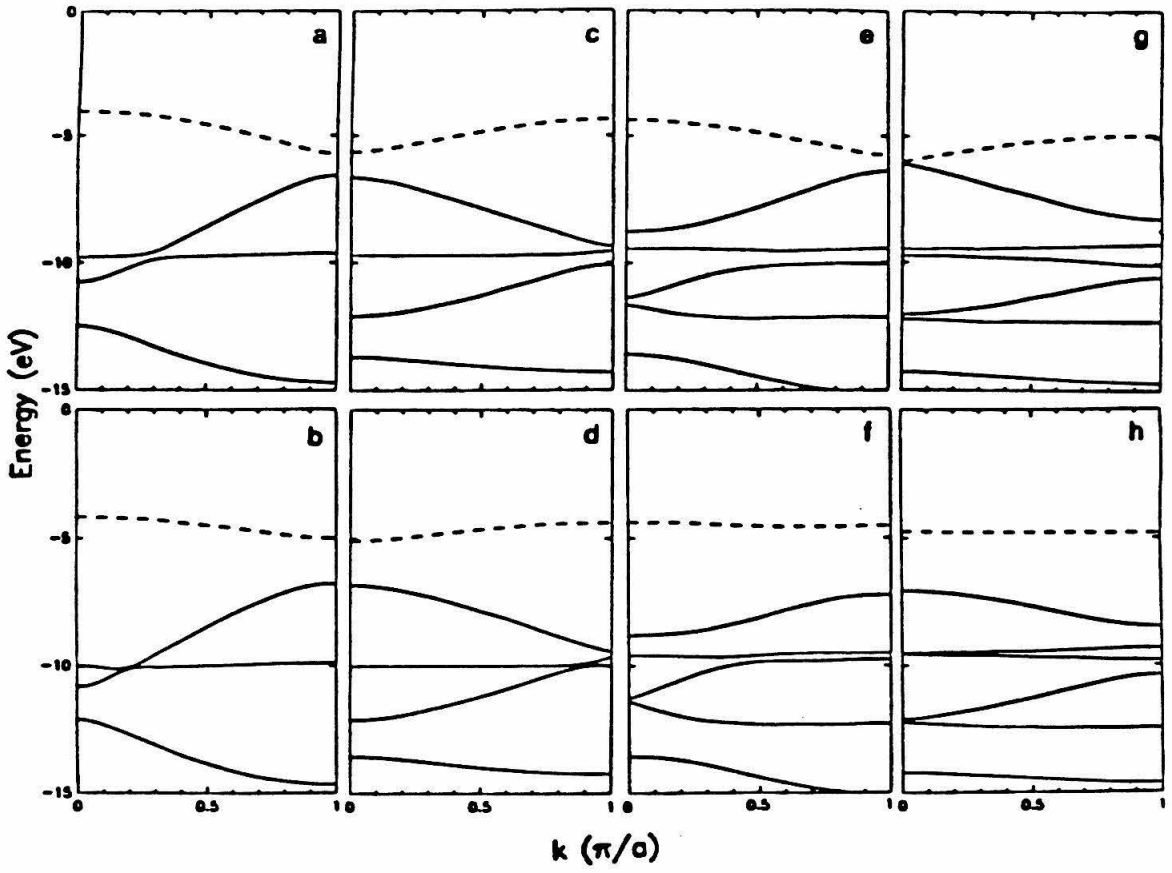


Figure 8. VEH band structures of (a) fulvenoid **4**, (b) quinoid **4**, (c) fulvenoid **5**, (d) quinoid **5**, (e) fulvenoid **6**, (f) quinoid **6**, (g) fulvenoid **7**, and (h) quinoid **7**. Only the π bands are shown. Dashed lines indicate the lowest unoccupied π band.

Table III. Results of band structure calculations (eV).

Polymer	Energy/Unit Cell[a]	IP[b,c]	E_g[b]	BW[b]
4 (fulvenoid)	–497.00	4.68	0.87	3.21
4 (quinoid)	–497.21	4.90	1.80	3.26
5 (fulvenoid)	–675.84	4.74	0.98	2.72
5 (quinoid)	–676.05	4.93	1.74	2.61
6 (fulvenoid)	–804.63	4.49	0.65	2.37
6 (quinoid)	–804.31	5.34	2.69	1.58
7 (fulvenoid)	–995.53	4.20	0.05	2.15
7 (quinoid)	–995.74	5.17	2.26	1.41
1		5.39	1.77	2.26
3		4.60	0.54	2.61
2		4.14	3.45	3.67
8		3.27	1.06	3.70

[a]From EHCO calculations. [b]From VEH calculations. [c]1.9 eV subtracted from calculated values.[16]

In fulvene, the HOMO in A and the LUMO is S, as discussed above. The A orbital has bonding interactions between pairs of atoms that are connected by double bonds. Transformation to a quinoid structure shifts most of the double bonds to pairs of atoms having *antibonding* interactions. Thus, the quinoid contribution destabilizes this orbital. In contrast, the S orbital (LUMO) of fulvene has double bonds between pairs of atoms having antibonding interactions. The shift to a quinoid structure places double bonds between atoms having bonding interactions. This orbital is therefore stabilized by quinoid contributions.

In this context, the VEH band structures of these materials are easily understood. In the fulvenoid geometry, the valence and conduction bands of **4** can be directly related to the HOMO and LUMO along the lines discussed above. In the quinoid structure, the intercell interactions are much stronger because they correspond to double bonds, and this perturbs the band structure. At the zone center (k=0), disregarding the weakly avoided crossing between the valence band and the very narrow second filled band, the composition of the valence and conduction bands are the same as in the fulvenoid geometry. That is, the valence band correlate to the HOMO of fulvene and the conduction band to the LUMO. At the zone edge ($k=\pi/a$), because of very strong quinoid contributions, the HOCO and LUCO have changed character compared to the HOCO and LUCO of the fulvenoid form. The HOCO now correlates with the LUMO of fulvene, and the LUCO with the HOMO. (Inspection of the coefficients of the VEH crystal orbitals confirms this analysis.) This requires a crossing between the valence and conduction bands. The crossing is apparently fairly strongly avoided; no turnaround is visible in the band structure.

A similar analysis holds for polyfulvene-vinylene (**5**). In this case, however, the crossing between the valence and conduction bands occurs in the *fulvenoid* form. The HOCO and LUCO of the fulvenoid form of **5** correlate with the LUMO and HOMO of

trimethylenecyclopentene (Figure 6), respectively. In the quinoid form, no band crossing occurs, and the entire valence (conduction) band correlates with the HOMO (LUMO) of trimethylenecyclopentene.

From this starting point, the effect of benzannelation can be rationalized readily. One can think of the conversion of **4** to **6** as resulting from the fusion 1,3-butadiene to each unit cell of **4** (Figure 9). The important orbitals of butadiene are its HOMO and LUMO, which are A and S, respectively. In Figure 9, we show the mixing of these orbitals with the HOCO and LUCO of **4**. It can be seen that this mixing provides a mechanism for closing the band gap. In fact, the mixing is strong enough to reverse the HOCO/LUCO ordering, and in **6** in the fulvenoid form the HOCO is S and the LUCO is A. Thus, benzannelation of **4** in the fulvenoid geometry induces an avoided valence band–conduction band crossing exactly analogous to the one seen in the quinoid form of **4**.

In the quinoid form of **4**, the band crossing has already occurred even before benzannelation. As shown in Figure 9, benzannelation can only increase E_g, and indeed this is the case. All the effects of benzannelation listed in Table III can be rationalized using the simple model of Figure 9. Exactly analogous arguments apply to the conversion of **5** to **7**. Apparently, the balance of effects in **7** is such that the HOCO and LUCO become almost degenerate, producing a *very* small band gap.

We note that these arguments are somewhat different from those of Brédas and co-workers concerning the conversion of polythiophene to polyisothianaphthene.[7] As mentioned above, in **1** there is a strong intrinsic preference for what we have termed the fulvenoid geometry, because thiophene enjoys an aromatic stabilization at this geometry. Thus, we would analyze the **1**→**3** conversion in terms of the left-hand side of Figure 9. The only difference is that E_g in **1** is larger than in **4**, as discussed above. The actual

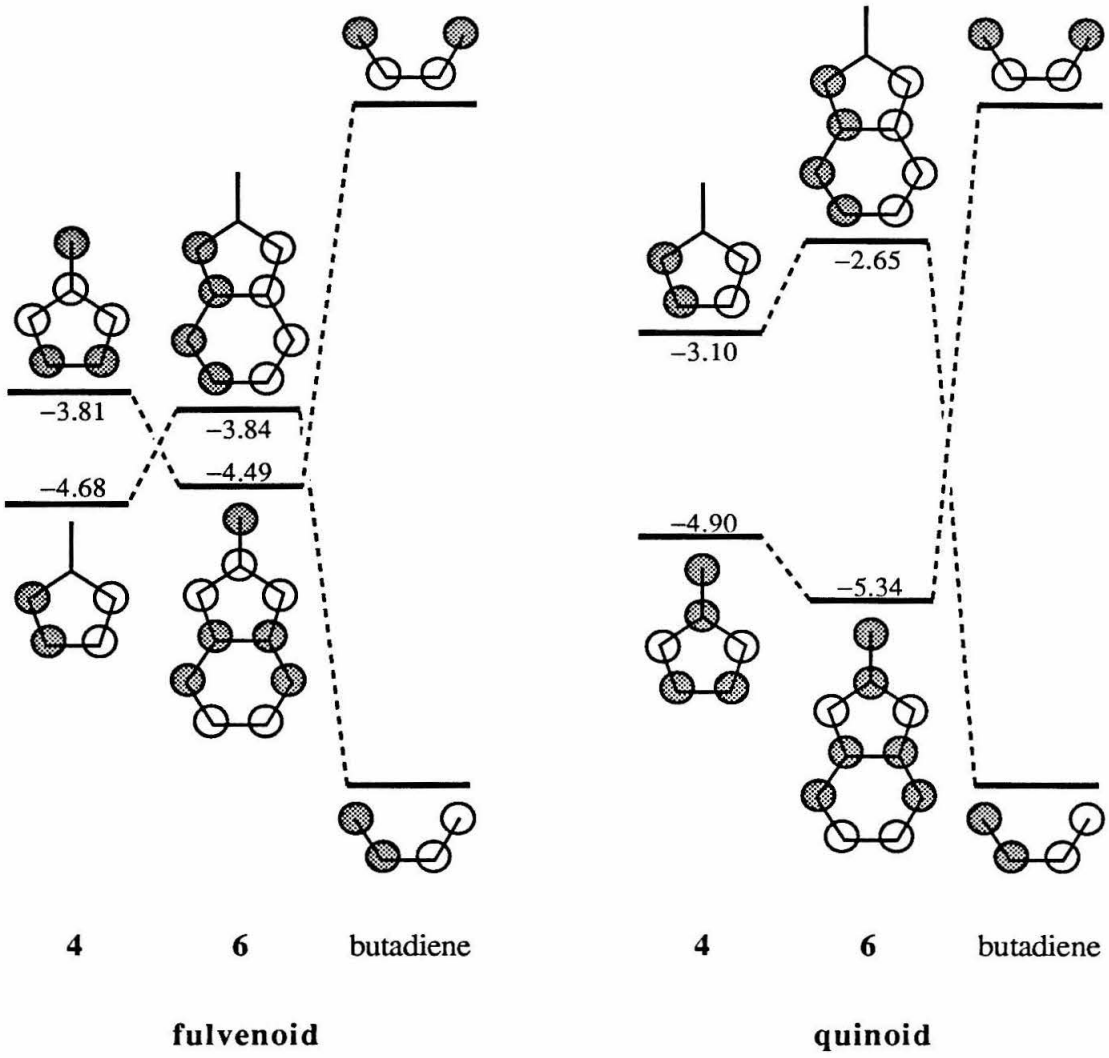


Figure 9. Orbital mixing diagram for the benzannelation of polyfulvene. Orbital energies (in eV) are from VEH calculations.

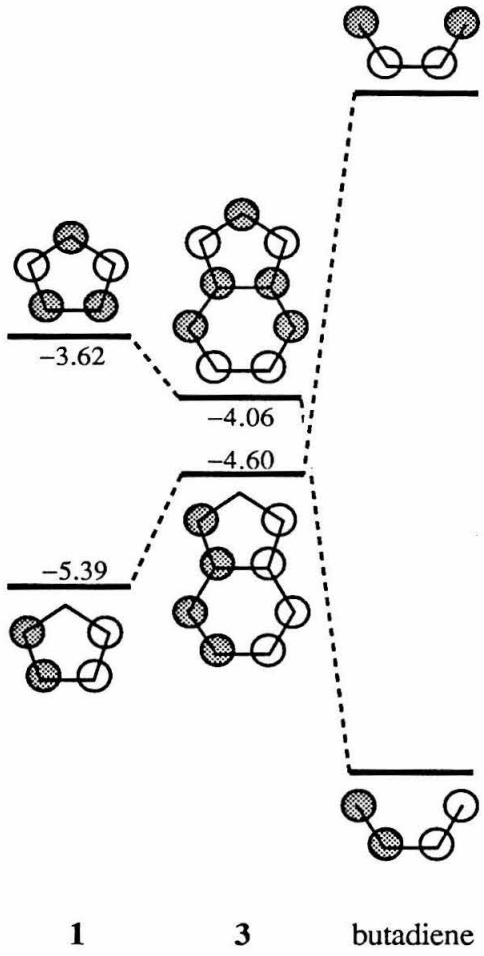


Figure 10. Orbital mixing diagram for the benzannelation of polythiophene. Orbital energies (in eV) are from VEH calculations.

mixing is shown in Figure 10. Again, E_g is reduced by benzannelation (in a "fulvenoid" geometry), but no crossing occurs because of the larger initial E_g.

The earlier work[7] concluded that the substantial diminution in E_g that occurs on going from **1** to **3** (and a similar effect in the monomers) is a consequence of increased quinoid contribution to the electronic structure. Earlier work has shown that *geometrical* distortions toward a quinoid form provide a mechanism for closing E_g in **1**.[22] (This can be rationalized in a way analogous to our treatment of fulvenoid/quinoid polyfulvene presented above.) On this basis, the observation of a smaller E_g in **3** was interpreted as resulting from "quinoid contributions to the *electronic* structure". This terminology is misleading, especially considering that benzannelation of thiophene does not produce the *geometrical* change indicative of increased quinoid character.[6] The calculated difference between C–C single and double bond lengths is 0.088 Å in thiophene; in isothianaphthene, this value increases to 0.102 Å. In a structure with more quinoid character this number should be smaller. We believe that the schemes of Figures 9 and 10 present a clearer view of the electronic changes that occur upon benzannelation.

In Table III we also show the consequence on converting polypyrrole (**2**) to polyisobenzopyrrole (**8**). Again, a substantial reduction in E_g occurs due to effects exactly analogous to the thiophene system.

We note that this analysis can be pursued further. One can "prepare" fulvenoid **4** by adding an ethylene end-on to each unit cell in cis-transoid polyacetylene (Figure 11, left). The HOCO is not affected by this addition, since it is forbidden by symmetry to mix with the orbitals of ethylene. In fact, when a VEH calculation on polyacetylene at the geometry of **4** is performed, the resulting HOCO energy is exactly the same as the HOCO energy of **4**. On the other hand, the LUCO of polyacetylene can interact with the ethylene orbitals. As seen in Figure 11, the resulting LUCO of **4** is just the in-phase combination of the polyacetylene LUCO with the π^* orbital of ethylene. This explains one additional

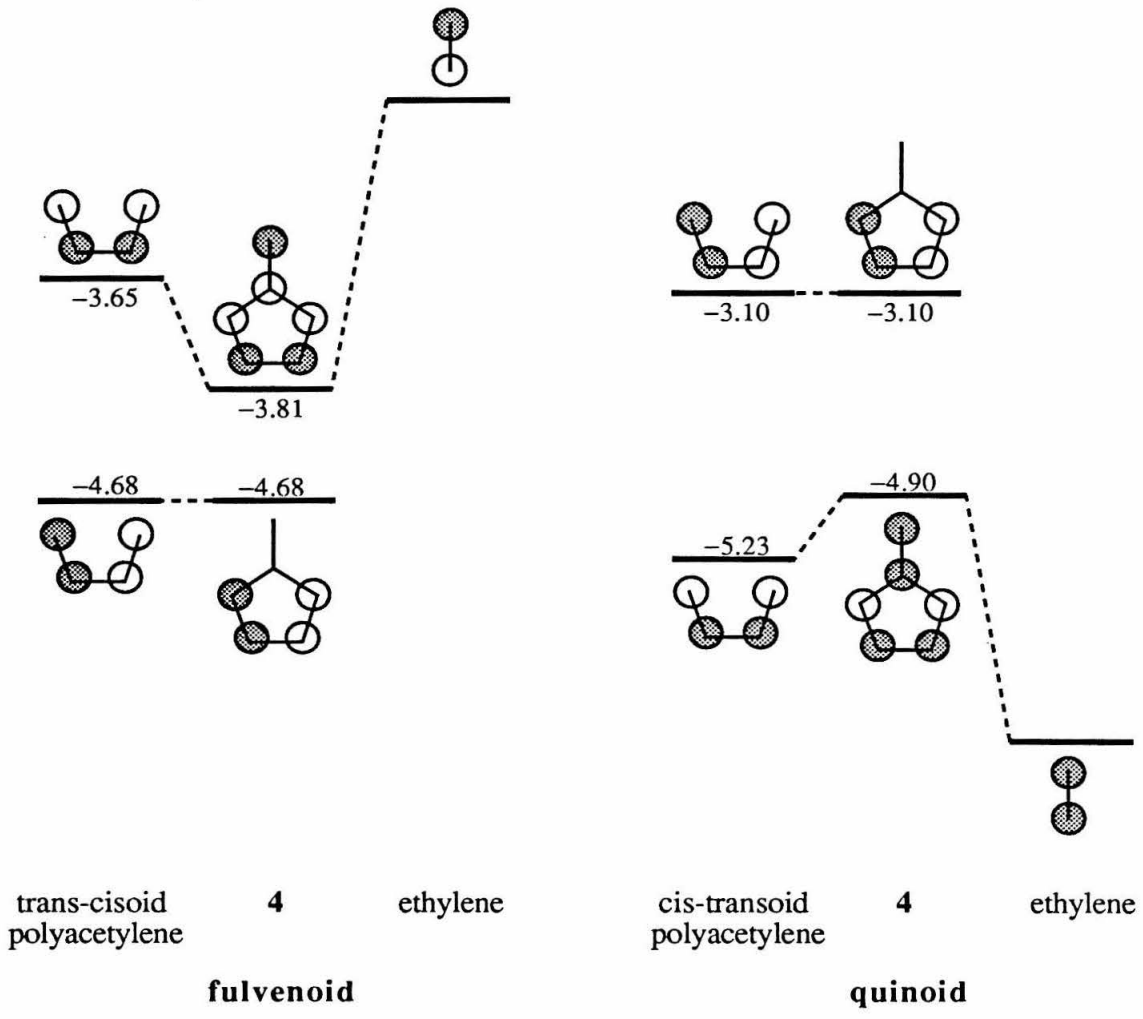


Figure 11. Orbital mixing diagram for the formation of polyfulvene from polyacetylene. Orbital energies (in eV) are from VEH calculations.

feature of polyfulvene. While we invoked the vanishing E_g at the HMO level to explain the smaller E_g in **4** when compared to **1**, **4** also has a significantly smaller E_g than polyacetylene (E_g=1.4 eV; Figure 1), which also shows the same HMO degeneracy. Figure 11 provides an explanation of this effect. Compared to polyacetylene, the HOCO of **4** has the same energy, while the LUCO has a lower energy, resulting in the lower E_g.

The same analysis can also be applied to quinoid polyfulvene (Figure 11, right). In this case, one starts with cis-transoid polyacetylene, and it is the HOCO that interacts with the orbitals of ethylene, while the LUCO remains unchanged. Furthermore, the HOCO starts out at a lower energy, so it interacts with the π orbital of ethylene, instead of π^*. This interaction raises the HOCO energy; thus, E_g also decreases. (That the resulting E_g is *larger* than the polyacetylene E_g of 1.4 eV is because the 1.4 eV value is obtained for trans polyacetylene, not the cis-transoid form considered here.)

Similarly, **1** and **2** can be obtained by mixing an S atom or NH group with trans-cisoid polyacetylene. This is shown for **1** in Figure 12. Note that the HOCO is lowered even in the absence of any interaction with S orbitals. This is an artifact of the VEH method which uses different parameters for carbons bonded to heteroatoms (Table II). When the polyacetylene calculation is performed with the C(-S) parameters, the HOCO has exactly the same energy as polythiophene HOCO.

As discussed above, the feasible target molecules for synthesis are **5** and **7**. As summarized in Table III, these polymers should have quite intriguing properties, if they adopt the fulvenoid geometry. The quinoid geometry, on the other hand, produces much less promising materials. Results of the EHCO calculations suggest that the two forms are quite close in energy. A more accurate estimate of relative energies would require extensive geometry optimizations on a high oligomer, which are not currently feasible. This is especially true for the quinoid form, for which there is no simple dimer or trimer structure without severe end-group perturbations. Rather than attempt such optimizations,

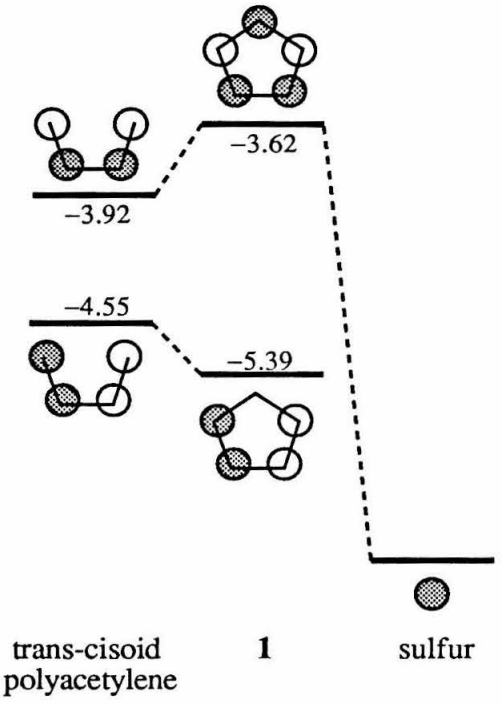


Figure 12. Orbital mixing diagram for the formation of polythiophene from polyacetylene. Orbital energies (in eV) are from VEH calculations.

we have chosen to emphasize the limiting forms (fulvenoid and quinoid), which most clearly illustrate the fundamental bonding principles. It is perhaps safe to anticipate that in the benzologue (**7**) the quinoid form would be preferred, because it allows the six-membered ring to be aromatic. (However, the data in Table III suggest that in the benzologue **6** the *fulvenoid* form is preferred, in contrast to the other polymers.)

While it is difficult to predict the structures of **5** and **7** in the undoped state, it seems certain that doping will favor the fulvenoid structures. That is, oxidative (reductive) doping always leads to distortions toward the structure with the higher (lower) energy HOCO (LUCO),[23] and that is the fulvenoid structure. We thus conclude that **5** and **7** could be quite promising materials.

Conclusions

At the HMO level, polyfulvene exhibits a HOCO/LUCO degeneracy exactly analogous to the degeneracy seen in polyacetylene. Also like polyacetylene, Peierls distortions can produce two structures that are, to first order, degenerate. When higher order effects are included, the two forms, which we have termed fulvenoid and quinoid, will not be degenerate, but our calculations indicate that they are quite close in energy. VEH calculations indicate that **5** should have properties that compare quite favorably with the known conducting polymers polypyrrole and polythiophene.

An analysis of the band structures of the benzo-fused compounds **6** and **7** suggests a new model for the effects of benzannelation in these and related structures. Rather than consider possible geometrical distortions, we emphasize the intrinsic electronic structures of these materials, using straightforward orbital-mixing arguments analogous to those used so frequently in molecular systems. All the consequences of benzannelation are rationalized by this model. The quantitative (VEH) calculations

indicate that **7** could have a very small band gap, making it an interesting experimental target.

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Appendix A: Cartesian Coordinates

Complete geometry specifications of the polymers discussed in this chapter are given in the following pages. They are in the form of cartesian coordinates rather than Z-matrices, because the VEH program accepts geometry information only in cartesian coordinate format. The atomic symbol is followed by the x, y, and z coordinates (in angstroms). "TV" indicates the translation vector, i.e., the length and orientation of the unit cells.

4 (fulvenoid):

C	0.0000	0.0000	0.0000
C	1.3448	0.0000	0.0000
C	2.2583	-1.1786	0.0000
C	2.2583	1.1786	0.0000
C	3.5515	-0.7382	0.0000
C	3.5515	0.7382	0.0000
H	-0.5964	-0.9116	0.0000
H	-0.5964	0.9116	0.0000
H	4.4536	-1.3352	0.0000
H	4.4536	1.3352	0.0000
C	4.0970	3.7628	0.0000
C	2.7522	3.7628	0.0000
C	1.8387	2.5842	0.0000
C	1.8387	4.9414	0.0000
C	0.5455	3.0246	0.0000
C	0.5455	4.5010	0.0000
H	4.6934	2.8512	0.0000
H	4.6934	4.6744	0.0000
H	-0.3566	2.4276	0.0000
H	-0.3566	5.0980	0.0000
TV	0.0000	7.5256	0.0000

4 (quinoid):

C	0.0000	0.0000	0.0000
C	1.3477	0.0000	0.0000
C	2.2395	-1.2056	0.0000
C	2.2395	1.2056	0.0000
C	3.6280	-0.6787	0.0000
C	3.6280	0.6787	0.0000
H	-0.6050	-0.9049	0.0000
H	-0.6050	0.9049	0.0000
H	4.4985	-1.3242	0.0000
H	4.4985	1.3242	0.0000
C	4.1361	3.7186	0.0000
C	2.7884	3.7186	0.0000
C	1.8966	2.5130	0.0000
C	1.8966	4.9242	0.0000
C	0.5081	3.0399	0.0000
C	0.5081	4.3973	0.0000
H	4.7411	2.8137	0.0000
H	4.7411	4.6235	0.0000
H	-0.3624	2.3944	0.0000
H	-0.3624	5.0428	0.0000
TV	0.0000	7.4372	0.0000

5 (fulvenoid):

C	0.0000	0.0000	0.0000
C	1.3448	0.0000	0.0000
C	2.2583	-1.1786	0.0000
C	2.2583	1.1786	0.0000
C	3.5515	-0.7382	0.0000
C	3.5515	0.7382	0.0000
H	-0.5964	-0.9116	0.0000
H	-0.5964	0.9116	0.0000
H	4.4536	-1.3352	0.0000
H	4.4536	1.3352	0.0000
C	1.8124	-2.2574	0.0000

C	1.8124	2.2574	0.0000
H	0.7312	-2.7121	0.0000
H	0.7312	2.7121	0.0000
C	4.4278	6.2419	0.0000
C	3.0830	6.2419	0.0000
C	2.1695	5.0633	0.0000
C	2.1695	7.4205	0.0000
C	0.8763	5.5037	0.0000
C	0.8763	6.9801	0.0000
H	5.0242	5.3303	0.0000
H	5.0242	7.1535	0.0000
H	-0.0258	4.9067	0.0000
H	-0.0258	7.5771	0.0000
C	2.6154	3.6679	0.0000
C	2.6154	8.8159	0.0000
H	3.6966	3.5298	0.0000
H	3.6966	8.9540	0.0000
TV	0.0000	12.4838	0.0000

5 (quinoid):

C	0.0000	0.0000	0.0000
C	1.3477	0.0000	0.0000
C	2.2395	-1.2056	0.0000
C	2.2395	1.2056	0.0000
C	3.6280	-0.6787	0.0000
C	3.6280	0.6787	0.0000
H	-0.6050	-0.9049	0.0000
H	-0.6050	0.9049	0.0000
H	4.4985	-1.3242	0.0000
H	4.4985	1.3242	0.0000
C	1.8966	-2.5131	0.0000
C	1.8966	2.5131	0.0000
H	0.8242	-2.7080	0.0000
H	0.8242	2.7080	0.0000
C	4.7243	6.1636	0.0000
C	3.3766	6.1636	0.0000
C	2.4848	4.9580	0.0000
C	2.4848	7.3692	0.0000
C	1.0963	5.4849	0.0000
C	1.0963	6.8423	0.0000
H	5.3293	5.2587	0.0000
H	5.3293	7.0685	0.0000
H	0.2258	4.8394	0.0000
H	0.2258	7.4878	0.0000
C	2.8277	3.6505	0.0000
C	2.8277	8.6767	0.0000
H	3.9001	3.4556	0.0000
H	3.9001	8.8716	0.0000
TV	0.0000	12.3272	0.0000

6 (fulvenoid):

C	0.0000	0.0000	0.0000
C	1.3471	0.0000	0.0000
C	2.2506	-1.1825	0.0000
C	2.2506	1.1825	0.0000
C	3.5532	-0.7488	0.0000
C	3.5532	0.7488	0.0000
H	-0.5961	-0.9118	0.0000

H	-0.5961	0.9118	0.0000
C	4.8304	-1.4448	0.0000
C	4.8304	1.4448	0.0000
C	5.9925	-0.7300	0.0000
C	5.9925	0.7300	0.0000
H	4.8306	-2.5351	0.0000
H	4.8306	2.5351	0.0000
H	6.9614	-1.2314	0.0000
H	6.9614	1.2314	0.0000
C	4.0719	3.7677	0.0000
C	2.7248	3.7677	0.0000
C	1.8213	2.5852	0.0000
C	1.8213	4.9502	0.0000
C	0.5187	3.0189	0.0000
C	0.5187	4.5165	0.0000
H	4.6680	2.8559	0.0000
H	4.6680	4.6795	0.0000
C	-0.7585	2.3229	0.0000
C	-0.7585	5.2125	0.0000
C	-1.9206	3.0377	0.0000
C	-1.9206	4.4977	0.0000
H	-0.7587	1.2326	0.0000
H	-0.7587	6.3028	0.0000
H	-2.8895	2.5363	0.0000
H	-2.8895	4.9991	0.0000
TV	0.0000	7.5354	0.0000

6 (quinoid):

C	0.0000	0.0000	0.0000
C	1.3485	0.0000	0.0000
C	2.2274	-1.2134	0.0000
C	2.2274	1.2134	0.0000
C	3.6264	-0.7185	0.0000
C	3.6264	0.7185	0.0000
H	-0.6073	-0.9034	0.0000
H	-0.6073	0.9034	0.0000
C	4.8414	-1.4191	0.0000
C	4.8414	1.4191	0.0000
C	6.0575	-0.7004	0.0000
C	6.0575	0.7004	0.0000
H	4.8721	-2.5086	0.0000
H	4.8721	2.5086	0.0000
H	7.0020	-1.2460	0.0000
H	7.0020	1.2460	0.0000
C	4.0626	3.7230	0.0000
C	2.7141	3.7230	0.0000
C	1.8352	2.5096	0.0000
C	1.8352	4.9364	0.0000
C	0.4362	3.0045	0.0000
C	0.4362	4.4415	0.0000
H	4.6699	2.8196	0.0000
H	4.6699	4.6264	0.0000
C	-0.7788	2.3039	0.0000
C	-0.7788	5.1421	0.0000
C	-1.9949	3.0226	0.0000
C	-1.9949	4.4234	0.0000
H	-0.8095	1.2144	0.0000
H	-0.8095	6.2316	0.0000

H	-2.9394	2.4770	0.0000
H	-2.9394	4.9690	0.0000
TV	0.0000	7.4460	0.0000

7 (fulvenoid):

C	0.0000	0.0000	0.0000
C	1.3470	0.0000	0.0000
C	2.2508	-1.1821	0.0000
C	2.2508	1.1821	0.0000
C	3.5536	-0.7487	0.0000
C	3.5536	0.7487	0.0000
H	-0.5963	-0.9112	0.0000
H	-0.5963	0.9112	0.0000
C	4.8311	-1.4452	0.0000
C	4.8311	1.4452	0.0000
C	5.9928	-0.7305	0.0000
C	5.9928	0.7305	0.0000
H	4.8311	-2.5352	0.0000
H	4.8311	2.5352	0.0000
H	6.9614	-1.2326	0.0000
H	6.9614	1.2326	0.0000
C	1.7956	-2.5746	0.0000
C	1.7956	2.5746	0.0000
H	0.7135	-2.7055	0.0000
H	0.7135	2.7055	0.0000
C	4.3870	6.2484	0.0000
C	3.0400	6.2484	0.0000
C	2.1362	5.0663	0.0000
C	2.1362	7.4305	0.0000
C	0.8334	5.4997	0.0000
C	0.8334	6.9971	0.0000
H	4.9833	5.3372	0.0000
H	4.9833	7.1597	0.0000
C	-0.4441	4.8032	0.0000
C	-0.4441	7.6936	0.0000
C	-1.6058	5.5179	0.0000
C	-1.6058	6.9789	0.0000
H	-0.4441	3.7132	0.0000
H	-0.4441	8.7836	0.0000
H	-2.5744	5.0159	0.0000
H	-2.5744	7.4900	0.0000
C	2.5913	3.6738	0.0000
C	2.5913	8.8230	0.0000
H	3.6735	3.5429	0.0000
H	3.6735	8.9540	0.0000
TV	0.0000	12.4968	0.0000

7 (quinoid):

C	0.0000	0.0000	0.0000
C	1.3490	0.0000	0.0000
C	2.2274	-1.2134	0.0000
C	2.2274	1.2134	0.0000
C	3.6263	-0.7181	0.0000
C	3.6263	0.7181	0.0000
H	-0.6074	-0.9039	0.0000
H	-0.6074	0.9039	0.0000
C	4.8404	-1.4191	0.0000

C	4.8404	1.4191	0.0000
C	6.0567	-0.6998	0.0000
C	6.0567	0.6998	0.0000
H	4.8709	-2.5087	0.0000
H	4.8709	2.5387	0.0000
H	7.0015	-1.2453	0.0000
H	7.0015	1.2453	0.0000
C	1.8360	-2.5097	0.0000
C	1.8360	2.5097	0.0000
H	0.7572	-2.6651	0.0000
H	0.7572	2.6651	0.0000
C	4.5608	6.1902	0.0000
C	3.2118	6.1902	0.0000
C	2.3335	4.9768	0.0000
C	2.3335	7.4037	0.0000
C	0.9348	5.4721	0.0000
C	0.9348	6.9083	0.0000
H	5.1682	5.2863	0.0000
H	5.1682	7.0941	0.0000
C	-0.2796	4.7711	0.0000
C	-0.2796	7.6093	0.0000
C	-1.4958	5.4904	0.0000
C	-1.4958	6.8900	0.0000
H	-0.3100	3.6816	0.0000
H	-0.3100	8.6989	0.0000
H	-2.4407	4.9449	0.0000
H	-2.4407	7.4355	0.0000
C	2.7248	3.6806	0.0000
C	2.7248	8.7000	0.0000
H	3.8037	3.5251	0.0000
H	3.8037	8.8553	0.0000
TV	0.0000	12.3804	0.0000

1:

S	1.0000	0.0000	0.0000
CS	-0.1556	-1.2523	0.0000
CS	-0.1556	1.2523	0.0000
C	-1.4305	-0.7242	0.0000
C	-1.4305	0.7242	0.0000
H	-2.3527	-1.2959	0.0000
H	-2.3527	1.2959	0.0000
S	-0.8721	3.8802	0.0000
CS	0.2834	2.6279	0.0000
CS	0.2834	5.1325	0.0000
C	1.5584	3.1560	0.0000
C	1.5584	4.6044	0.0000
H	2.4805	2.5843	0.0000
H	2.4805	5.1762	0.0000
TV	0.0000	7.7605	0.0000

3:

S	1.0000	0.0000	0.0000
CS	-0.1474	-1.2326	0.0000
CS	-0.1474	1.2326	0.0000
C	-1.4334	-0.7403	0.0000
C	-1.4334	0.7403	0.0000
C	-2.7073	-1.4391	0.0000
C	-2.7073	-1.4391	0.0000

C	-3.8751	-0.7305	0.0000
C	-3.8751	-0.7305	0.0000
H	-2.7044	-2.5291	0.0000
H	-2.7044	2.5291	0.0000
H	-4.8406	-1.2385	0.0000
H	-4.8406	1.2385	0.0000
S	-0.8618	3.8428	0.0000
CS	0.2856	2.6102	0.0000
CS	0.2856	5.0754	0.0000
C	1.5716	3.1025	0.0000
C	1.5716	4.5830	0.0000
C	2.8455	2.4036	0.0000
C	2.8455	5.2819	0.0000
C	4.0133	3.1123	0.0000
C	4.0133	4.5732	0.0000
H	2.8426	1.3136	0.0000
H	2.8426	6.3719	0.0000
H	4.9788	2.6043	0.0000
H	4.9788	5.0812	0.0000
TV	0.0000	7.6855	0.0000

2:

H	0.0000	0.0000	0.0000
N	0.9930	0.0000	0.0000
CN	1.7969	-1.1438	0.0000
CN	1.7969	1.1438	0.0000
C	3.1258	-0.7197	0.0000
C	3.1258	0.7197	0.0000
H	4.0018	-1.3514	0.0000
H	4.0018	1.3514	0.0000
H	2.9832	3.6028	0.0000
N	1.9902	3.6028	0.0000
CN	1.1864	2.4590	0.0000
CN	1.1864	4.7465	0.0000
C	-0.1426	2.8831	0.0000
C	-0.1426	4.3224	0.0000
H	-1.0186	2.2524	0.0000
H	-1.0186	4.9542	0.0000
TV	0.0000	7.2055	0.0000

8:

H	0.0000	0.0000	0.0000
N	0.9930	0.0000	0.0000
CN	1.7969	-1.1438	0.0000
CN	1.7969	1.1438	0.0000
C	3.1258	-0.7197	0.0000
C	3.1258	0.7197	0.0000
C	4.3947	-1.4317	0.0000
C	4.3947	1.4317	0.0000
C	5.5626	-0.7272	0.0000
C	5.5626	0.7272	0.0000
H	4.3814	-2.5216	0.0000
H	4.3814	2.5216	0.0000
H	6.5268	-1.2377	0.0000
H	6.5268	1.2377	0.0000
H	2.9832	3.6028	0.0000
N	1.9902	3.6028	0.0000
CN	1.1864	2.4590	0.0000

CN	1.1864	4.7465	0.0000
C	-0.1426	2.8831	0.0000
C	-0.1426	4.3224	0.0000
C	-1.4115	2.1711	0.0000
C	-1.4115	5.0345	0.0000
C	-2.5794	2.8756	0.0000
C	-2.5794	4.3299	0.0000
H	-1.3982	1.0811	0.0000
H	-1.3982	6.1244	0.0000
H	-3.5436	2.3651	0.0000
H	-3.5426	4.8404	0.0000
TV	0.0000	7.2055	0.0000

Appendix B: Listing of Computer Programs

On the following pages the source listings of the programs used to perform the band structure calculations are given. POLYHMO is the "standard" HMO program for one-dimensional polymers, while POLYHMO2 allows the user to modify the Hückel matrix, allowing calculations on systems with heteroatoms, as well as bond alternation. VEH is the program to perform valence effective hamiltonian calculations.

```
C Program POLYHMO
C
C Written by Julianto Pranata, California Institute of Technology,
C April 1986. Revised April 1987.
C
C This is a program for calculating band structures of linear conjugated
C hydrocarbon polymers in the Huckel approximation. It constructs a
C Huckel matrix between Bloch functions and solves it at eleven
C equally spaced points in the Brillouin zone of the polymer (0<k<pi/a).
C
C The input deck is a file called POLYHMO.IN; it consists of:
C  1. Title
C  2. Subtitle
C  3. Number of atoms in a unit cell
C  4. Connectivities between atoms inside a unit cell (i.e. "i,j"
C     indicates that atoms i and j are nearest neighbors in the unit
C     cell). Terminates with "0,0"
C  5. Connectivities between atoms in adjacent unit cells. Supposing
C     atom i is connected to atom j in the left adjacent unit cell,
C     the line would read "i,j,-1". If j is in the right adjacent unit
C     cell, it reads "i,j,1". Terminates with "0,0,0"
C
C The program calls on the subroutine EIGCH which can be found in the
C IMSL Math library. The subroutine performs diagonalization of a
C complex Hermitian matrix.
C
C The energy eigenvalues are expressed in units of beta; the zero of
C energy is taken to be alpha. It is worthwhile to remember that beta
C is a negative quantity.
C
C The program produces two output files. One, POLYHMO.OUT, contains
C the information about eigenvalues, eigenvectors, and the
C performance index of the diagonalization. The other, SPLINE.IN,
C acts as the input for the interpolation program SPLINE3.
C In the SPLINE.IN file, the energies are the negative of those in
C POLYHMO.OUT; this is to reflect the fact that beta is negative.
C
C Reference:
C
C Albright, T.A.; Burdett, J.K.; Whangbo, M.H. "Orbital Interactions
C in Chemistry", Wiley, New York, 1985. Chapter 13.
C
C Below is a sample input deck for POLYHMO.
C
C Polyacene
C HMO
C 4
C 1,2
C 2,3
C 3,4
C 0,0
C 1,2,-1
C 3,4,1
```

```
C 0,0,0
C
C=====================================================================
C
      CHARACTER*36 TITLE,SUBT
      COMPLEX H(210),Z(20,20)
      REAL TRA(20,20),TER(20,20),WK(500),D(20),E(20,11)
      DATA PI/3.141592654/
C
C     H      = HUCKEL MATRIX BETWEEN BLOCH ORBITALS. IN HERMITIAN
C              STORAGE MODE
C     D      = ENERGY EIGENVALUES; INDEX REFERS TO BAND
C     E      = MATRIX OF ENERGIES AS A FUNCTION OF K
C     WK     = WORK AREA (USED IN SUBROUTINE EIGCH)
C     Z      = EIGENVECTOR MATRIX
C     TRA    = CONNECTIVITY INSIDE UNIT CELL
C     TER    = CONNECTIVITY BETWEEN UNIT CELLS
C
C     INITIALIZE MATRICES
C
      DO 10 I=1,20
      DO 10 J=1,20
      TRA(I,J)=0.0
 10   TER(I,J)=0.0
      DO 11 I=1,210
 11   H(IN)=(0.0,0.0)
C
C     INPUT TITLE, COORDINATES, CONNECTIVITIES
C
      OPEN(2,FILE='POLYHMO.IN',STATUS='OLD')
      READ(2,15) TITLE
      READ(2,15) SUBT
 15   FORMAT(A36)
      READ(2,*) NAT
      OPEN(3,FILE='POLYHMO.OUT',STATUS='UNKNOWN')
      WRITE(3,32) TITLE
      WRITE(3,34) SUBT
 32   FORMAT(/1X,A36)
 34   FORMAT(1X,A36)
      WRITE(3,200)
 200  FORMAT(/1X,' Intracell connectivities:')
      DO 20 I=1,100
      READ(2,*) J,K
      IF(J.EQ.0) GOTO 21
      WRITE(3,201) J,K
 201  FORMAT(4X,2I4)
      TRA(J,K)=1.0
      TRA(K,J)=1.0
 20   CONTINUE
 21   WRITE(3,210)
 210  FORMAT(1X,' Intercell connectivities:')
      DO 30 I=1,100
      READ(2,*) J,K,L
```

```
      IF(J.EQ.0) GOTO 31
      WRITE(3,202) J,K,L
 202  FORMAT(4X,3I4)
      TER(J,K)=FLOAT(L)
      TER(K,J)=-TER(J,K)
 30   CONTINUE
 31   CONTINUE
C
C     LOOP OVER K-VALUES
C
      DO 100 K=1,11
      RK=(K-1)*PI/10.0
C
C     CONSTRUCT HUCKEL MATRIX
C
C     INTRACELL INTERACTIONS
C
      IN=0
      DO 40 I=1,NAT
      DO 40 J=1,I
      IN=IN+1
      IF(TRA(I,J).EQ.0) GOTO 40
      H(IN)=H(IN)+(1.0,0.0)
 40   CONTINUE
C
C     INTERCELL INTERACTIONS
C
      IN=0
      DO 50 I=1,NAT
      DO 50 J=1,I
      IN=IN+1
      IF(TER(I,J).EQ.0) GOTO 50
      H(IN)=H(IN)+COS(TER(I,J)*RK)*(1.0,0.0)+SIN(TER(I,J)*RK)*(0.0,1.0)
 50   CONTINUE
C
C     DIAGONALIZE HUCKEL MATRIX
C
      CALL EIGCH(H,NAT,2,D,Z,20,WK,IER)
      DO 101 I=1,NAT
 101  E(I,K)=-D(I)
C
C     WRITE OUT RESULTS
      RK=RK/PI
      WRITE(3,51) RK
 51   FORMAT(/' k = ',F6.4,' * pi/a')
      WRITE(3,52) IER,WK(1)
 52   FORMAT( ' IER =',I5,'      Performance index = ',E10.5)
      WRITE(3,53) (D(I),I=1,NAT)
 53   FORMAT(' Eigenvalues =', 4F10.6)
      DO 60 I=1,NAT
      WRITE(3,54) (Z(J,I),J=1,NAT)
 54   FORMAT(' Eigenvector ='/3X,4(F6.3,1X,F6.3,'i',3x))
 60   CONTINUE
```

```
C
C     RESET HUCKEL MATRIX TO ZERO
C
      IN=0
      DO 80 I=1,NAT
      DO 80 J=1,I
      IN=IN+1
 80   H(IN)=(0.0,0.0)
C
 100  CONTINUE
C
C     WRITE FILE FOR INPUT TO SPLINE FITTING PROGRAM
C
      OPEN(4,FILE='SPLINE.IN',STATUS='UNKNOWN')
      WRITE(4,110) TITLE
      WRITE(4,110) SUBT
      N11=11
      WRITE(4,111) NAT,N11
 110  FORMAT(A36)
 111  FORMAT('k (0-pi/a)'/'E(k)'/I2/I2)
      DO 120 I=1,NAT
      DO 120 K=1,11
      RK=FLOAT(K-1)/10
 120  WRITE(4,121) RK,E(I,K)
 121  FORMAT(F3.1,',',F10.6)
C
      STOP
      END
```

```
C Program POLYHMO2
C
C Written by Julianto Pranata, California Institute of Technology,
C May 1986. Revised April 1987.
C
C This program is an improvement on the original POLYHMO program, which
C is a program for calculating band structures of linear conjugated
C hydrocarbon polymers in the Huckel approximation. It constructs a
C Huckel matrix between Bloch functions and solves it at eleven
C equally spaced points in the Brillouin zone of the polymer (0<k<pi/a).
C
C The improved program has the additional capabilities of:
C  1. Calculating band structures of polymers containing the heteroatoms
C     N(sp2), N(sp3), O(sp2), O(sp3), using Streitwieser's parameters.
C  2. Modifying the Huckel matrix elements to simulate distortions
C     (bond alternations) or to calculate polymers containing other
C     heteroatoms.
C
C The input deck is a file called POLYHMO.IN; it consists of:
C  1. Title
C  2. Subtitle
C  3. No. of atoms in a unit cell
C  4. Number of sp2 nitrogens, sp3 nitrogens, sp2 oxygens, sp3
C     oxygens, in that order.
C  5. Numbers to tell the program which atoms are the heteroatoms.
C     A separate line is necessary for each type of heteroatom, but
C     a blank line is not necessary (nor allowed!) if the number of
C     a particular heteroatom is zero.
C  6. Connectivities between atoms inside a unit cell (i.e. "i,j"
C     indicates that atoms i and j are nearest neighbors in the unit
C     cell). Terminates with "0,0"
C  7. Connectivities between atoms in adjacent unit cells. Supposing
C     atom i is connected to atom j in the left adjacent unit cell,
C     the line would read "i,j,-1". If j is in the right adjacent unit
C     cell, it reads "i,j,1". Terminates with "0,0,0"
C  8. Modifications of the intracell matrix. "0" means no modification,
C     any other integer means there is a modification. The modification
C     is listed as in no. 7 except a third number, indicating the new
C     matrix element, is necessary. Terminates with "0,0,0"
C  9. Modifications of the intercell matrix. Same rules as above,
C     including the sign convention in no. 7.
C
C The program calls on the subroutine EIGCH which can be found in the
C IMSL Math library. The subroutine performs diagonalization of a
C complex Hermitian matrix.
C
C The energy eigenvalues are expressed in units of beta; the zero of
C energy is taken to be alpha. It is worthwhile to remember that beta
C is a negative quantity.
C
C The program produces two output files. One, POLYHMO.OUT, contains
C the information about eigenvalues, eigenvectors, and the
C performance index of the diagonalization. The other, SPLINE.IN,
```

```
C acts as the input for the interpolation program SPLINE3.
C In the SPLINE.IN file, the energies are the negative of those in
C POLYHMO.OUT; this is to reflect the fact that beta is negative.
C
C References:
C
C Albright, T.A.; Burdett, J.K.; Whangbo, M.H. "Orbital Interactions
C in Chemistry", Wiley, New York, 1985. Chapter 13.
C
C Streitwieser, A., Jr. "Molecular Orbital Theory for Organic Chemists,"
C Wiley, New York, 1961. Page 135.
C
C The sample input deck below is for the band structure calculation of
C polypyrrole, with carbon-carbon bond alternation.
C
C polypyrrole
C HMO
C 5
C 0,1,0,0
C 5
C 1,2
C 2,3
C 3,4
C 4,5
C 1,5
C 0,0
C 1,4,-1
C 0,0,0
C 1
C 1,2,1.1
C 2,3,0.9
C 3,4,1.1
C 0,0,0.0
C 1
C 1,4,-1
C 0,0,0
C
C=======================================================================
C
      CHARACTER*36 TITLE,SUBT
      COMPLEX H(210),Z(20,20)
      REAL X(20),TRA(20,20),TER(20,20),WK(500),D(20),E(20,11)
      INTEGER NNSP2N(9),NNSP3N(9),NNSP2O(9),NNSP3O(9)
      DATA PI/3.141592654/
C
C     H      = HUCKEL MATRIX BETWEEN BLOCH ORBITALS. IN HERMITIAN
C              STORAGE MODE
C     D      = ENERGY EIGENVALUES; INDEX REFERS TO BAND
C     E      = MATRIX OF ENERGIES AS A FUNCTION OF K
C     WK     = WORK AREA (USED IN SUBROUTINE EIGCH)
C     Z      = EIGENVECTOR MATRIX
C     TRA    = CONNECTIVITY INSIDE UNIT CELL
C     TER    = CONNECTIVITY BETWEEN UNIT CELLS
```

```
C
C     INITIALIZE MATRICES
C
      DO 10 I=1,20
      DO 10 J=1,20
      TRA(I,J)=0.0
 10   TER(I,J)=0.0
      DO 11 I=1,210
 11   H(IN)=(0.0,0.0)
      DO 12 I=1,9
      NNSP2N(I)=0
      NNSP3N(I)=0
      NNSP2O(I)=0
 12   NNSP3O(I)=0
C
C     INPUT TITLE, COORDINATES
C
      OPEN(2,FILE='POLYHMO.IN',STATUS='OLD')
      READ(2,15) TITLE
      READ(2,15) SUBT
 15   FORMAT(A36)
      READ(2,*) NAT
C
C     INPUT HETEROATOMS, SP2 NITROGENS, SP3 NITROGENS, SP2 OXYGENS,
C     SP3 OXYGENS, IN THAT ORDER
C
      READ(2,*) NSP2N,NSP3N,NSP2O,NSP3O
      MAX=MAX0(NSP2N,NSP3N,NSP2O,NSP3O)
      IF(NSP2N.EQ.0) GOTO 500
      READ(2,*) (NNSP2N(I),I=1,NSP2N)
 500  IF(NSP3N.EQ.0) GOTO 501
      READ(2,*) (NNSP3N(I),I=1,NSP3N)
 501  IF(NSP2O.EQ.0) GOTO 502
      READ(2,*) (NNSP2O(I),I=1,NSP2O)
 502  IF(NSP3O.EQ.0) GOTO 503
      READ(2,*) (NNSP3O(I),I=1,NSP3O)
 503  CONTINUE
C
C     WRITE OUTPUT FILE HEADER
C
      OPEN(3,FILE='POLYHMO.OUT',STATUS='UNKNOWN')
      WRITE(3,32) TITLE
      WRITE(3,34) SUBT
 32   FORMAT(/1X,A36)
 34   FORMAT(1X,A36)
      IF(NSP2N.EQ.0) GO TO 510
      WRITE(3,509) (NNSP2N(I),I=1,NSP2N)
 509  FORMAT(1X,' sp2 nitrogen atoms:',9I4)
 510  IF(NSP3N.EQ.0) GOTO 512
      WRITE(3,511) (NNSP3N(I),I=1,NSP3N)
 511  FORMAT(1X,' sp3 nitrogen atoms:',9I4)
 512  IF(NSP2O.EQ.0) GOTO 514
      WRITE(3,513) (NNSP2O(I),I=1,NSP2O)
```

```
 513  FORMAT(1X,' sp2 oxygen atoms  :',9I4)
 514  IF(NSP3O.EQ.0) GOTO 516
      WRITE(3,515) (NNSP3O(I),I=1,NSP3O)
 515  FORMAT(1X,' sp3 oxygen atoms  :',9I4)
 516  CONTINUE
C
C     INPUT CONNECTIVITES
C
      DO 20 I=1,100
      READ(2,*) J,K
      IF(J.EQ.0) GOTO 21
      TRA(J,K)=1.0
      DO 520 L=1,MAX
      IF((J.EQ.NNSP3N(L)).OR.(K.EQ.NNSP3N(L))) TRA(J,K)=0.8
      IF((J.EQ.NNSP3O(L)).OR.(K.EQ.NNSP3O(L))) TRA(J,K)=0.8
      IF((J.EQ.NNSP3N(L)).AND.(K.EQ.NNSP3O(L))) TRA(J,K)=0.7
      IF((K.EQ.NNSP3N(L)).AND.(J.EQ.NNSP3O(L))) TRA(J,K)=0.7
 520  CONTINUE
      TRA(K,J)=TRA(J,K)
 20   CONTINUE
 21   DO 30 I=1,100
      READ(2,*) J,K,L
      IF(J.EQ.0) GOTO 31
      TER(J,K)=FLOAT(L)
      DO 521 L=1,MAX
      IF((J.EQ.NNSP3N(L)).OR.(K.EQ.NNSP3N(L))) TER(J,K)=FLOAT(L)*0.8
      IF((J.EQ.NNSP3O(L)).OR.(K.EQ.NNSP3O(L))) TER(J,K)=FLOAT(L)*0.8
      IF((J.EQ.NNSP3N(L)).AND.(K.EQ.NNSP3O(L))) TER(J,K)=FLOAT(L)*0.7
      IF((J.EQ.NNSP3O(L)).AND.(K.EQ.NNSP3N(L))) TER(J,K)=FLOAT(L)*0.7
 521  CONTINUE
      TER(K,J)=-TER(J,K)
 30   CONTINUE
 31   CONTINUE
C
C     MODIFY DIAGONAL ELEMENTS
C
      DO 523 J=1,NAT
      DO 523 L=1,MAX
      IF(J.EQ.NNSP2N(L)) TRA(J,J)=0.5
      IF(J.EQ.NNSP3N(L)) TRA(J,J)=1.5
      IF(J.EQ.NNSP2O(L)) TRA(J,J)=1.0
      IF(J.EQ.NNSP3O(L)) TRA(J,J)=2.0
 523  CONTINUE
C
C     MODIFY HUCKEL MATRIX IF DESIRED
C
      READ(2,*) MODTRA
      IF(MODTRA.EQ.0) GOTO 530
      DO 529 I=1,100
      READ(2,*) J,K,TRA(J,K)
      IF(J.EQ.0) GOTO 530
 529  TRA(K,J)=TRA(J,K)
 530  READ(2,*) MODTER
```

```
      IF(MODTER.EQ.0) GOTO 532
      DO 531 I=1,100
      READ(2,*) J,K,TER(J,K)
      IF(J.EQ.0) GOTO 532
  531 TER(K,J)=-TER(J,K)
  532 CONTINUE
C
C     WRITE HUCKEL MATRICES FOR UNIT CELLS
C
      WRITE(3,1005)
      DO 1000 I=1,NAT
 1000 WRITE(3,1001) (TRA(I,J),J=1,NAT)
      WRITE(3,1006)
      DO 1003 I=1,NAT
 1003 WRITE(3,1001) (TER(I,J),J=1,NAT)
 1001 FORMAT(10F7.3)
 1005 FORMAT(/1X,' Intracell matrix:')
 1006 FORMAT(/1X,' Intercell matrix:')
C
C     LOOP OVER K-VALUES
C
      DO 100 K=1,11
      RK=(K-1)*PI/10.0
C
C     CONSTRUCT HUCKEL MATRIX
C
C     INTRACELL INTERACTIONS
C
      IN=0
      DO 40 I=1,NAT
      DO 40 J=1,I
      IN=IN+1
      IF(TRA(I,J).EQ.0) GOTO 40
      H(IN)=H(IN)+TRA(I,J)*(1.0,0.0)
   40 CONTINUE
C
C     INTERCELL INTERACTIONS
C
      IN=0
      DO 50 I=1,NAT
      DO 50 J=1,I
      IN=IN+1
      IF(TER(I,J).EQ.0) GOTO 50
      A=1.0
      IF(TER(I,J).LT.0) A=-1.0
      H(IN)=H(IN)+(COS(A*RK)*(1.0,0.0)+SIN(A*RK)*(0.0,1.0))*
     *ABS(TER(I,J))
   50 CONTINUE
C
C     DIAGONALIZE HUCKEL MATRIX
C
      CALL EIGCH(H,NAT,2,D,Z,20,WK,IER)
      DO 101 I=1,NAT
```

```
 101  E(I,K)=-D(I)
C
C     WRITE OUT RESULTS
      RK=RK/PI
      WRITE(3,51) RK
 51   FORMAT(/' k = ',F6.4,' * pi/a')
      WRITE(3,52) IER,WK(1)
 52   FORMAT( ' IER =',I5,'      Performance index = ',E10.5)
      WRITE(3,53) (D(I),I=1,NAT)
 53   FORMAT(' Eigenvalues =', 4F10.6)
      DO 60 I=1,NAT
      WRITE(3,54) (Z(J,I),J=1,NAT)
 54   FORMAT(' Eigenvector ='/3X,4(F6.3,1X,F6.3,'i',3x))
 60   CONTINUE
C
C     RESET HUCKEL MATRIX TO ZERO
C
      IN=0
      DO 80 I=1,NAT
      DO 80 J=1,I
      IN=IN+1
 80   H(IN)=(0.0,0.0)
C
 100  CONTINUE
C
C     WRITE FILE FOR INPUT TO SPLINE FITTING PROGRAM
C
      OPEN(4,FILE='SPLINE.IN',STATUS='UNKNOWN')
      WRITE(4,110) TITLE
      WRITE(4,110) SUBT
      N11=11
      WRITE(4,111) NAT,N11
 110  FORMAT(A36)
 111  FORMAT('k (0-pi/a)'/'E(k)'/I2/I2)
      DO 120 I=1,NAT
      DO 120 K=1,11
      RK=FLOAT(K-1)/10
 120  WRITE(4,121) RK,E(I,K)
 121  FORMAT(F3.1,',',F10.6)
C
      STOP
      END
```

```
C Program VEH
C
C Written by Julianto Pranata, California Institute of Technology,
C July 1986. Oxygen parameters added, January 1988.
C
C This program calculates the band structure of one-dimensional polymers
C using the Valence Effective Hamiltonian method. In this program, the
C summation over unit cells in constructing the potential energy and
C overlap matrices over Bloch orbitals are carried out up to the fourth
C neighboring unit cell. Band energies are calculated at eleven equidistant
C points in half of the first Brillouin zone of the polymer.
C
C The program is limited to translationally symmetric polymers. Maximum
C dimensions are 40 atoms and 100 valence orbitals per unit cell.
C
C The input file is assigned to FOR001 and is formatted as follows:
C
C  1. Title (A60)
C  2. Subtitle (A60)
C  3. Number of atoms per unit cell (free format)
C  4. List of atoms (left justified) and Cartesian coordinates (A2,3F9.5)
C  5. Translation vector in Cartesian coordinates (3F9.5)
C  6. Number of eigenvectors to print (free format)
C
C Parameters are available for C, H, N, O, and S. Different parameters are
C necessary for carbons bonded to heteroatoms, thus the atom list may
C contain symbols like "CS" and "CN" to indicate carbons bonded to S and N.
C
C The translation vector defines the length/orientation of the unit cell.
C
C The output file is assigned to FOR002. All the eigenvalues at eleven
C points in the first Brillouin zone are printed. However, only the lowest
C n eigenvectors are listed, n being specified in the input file. This
C avoids overly long output files, especially since this method does not
C give good results for the empty bands anyway.
C
C Another file (FOR003) is written containing the eigenvalues (energies).
C This may be useful input to a plotting program such as GENPLOT.
C
C The program is not able to detect band crossings, the eigenvalues and
C eigenvectors are given in ascending energy at each of the eleven points.
C Examination of the eigenvectors may be necessary to obtain a correct
C picture of the band structure.
C
C References:
C
C Bredas, J.L. et al. J. Chem. Phys. 75, 225 (1981) (Method and parameters
C   for C and H)
C Bredas, J.L. et al. J. Chem. Phys. 78, 5656 (1983) (Parameters for S)
C Bredas, J.L. et al. J. Chem. Phys. 78, 6137 (1983) (Parameters for N)
C
C Sample input deck (polyacetylene):
C
```

```
C Test of VEH
C Polyacetylene
C 4
C C    0.00000  0.00000  0.00000
C C    1.18400  0.64000  0.00000
C H    0.00000 -1.08000  0.00000
C H    1.18400  1.72000  0.00000
C    2.48000  0.00000  0.00000
C 5
C
C
      IMPLICIT REAL*8 (A-H,O-Z)
      CHARACTER*2 ATOM(40),ATOM2(100),ORB(100)
      DIMENSION TV(3)
      DIMENSION X(40),Y(40),Z(40)
      DIMENSION S(5,100,100),T(5,100,100),V(5,100,100),SF(9,100,200)
      DIMENSION E(100)
      COMPLEX*16 SB(100,100),F(100,100),C(100,100)
C
C      DEFINITION OF VARIABLES:
C       ATOM    = TYPE OF ATOM
C       X,Y,Z   = COORDINATES OF EACH ATOM IN THE UNIT CELL
C       TV      = TRANSLATION VECTOR, DEFINES SIZE/ORIENTATION OF UNIT CELL
C       S       = OVERLAP MATRIX BETWEEN ATOMIC ORBITALS. FIRST INDEX REFERS
C                 TO (J-1)TH NEIGHBOR MATRIX ELEMENT BEING CALCULATED.
C       T       = KINETIC ENERGY MATRIX ELEMENTS
C       V       = POTENTIAL ENERGY MATRIX ELEMENTS
C       SB      = OVERLAP MATRIX ELEMENTS BETWEEN BLOCH ORBITALS
C       F       = FOCK MATRIX ELEMENTS BETWEEN BLOCH ORBITALS
C       E       = EIGENVALUES OR THE BAND ENERGIES
C       C       = EIGENVECTORS
C
C
      CALL INPUT(N,ATOM,X,Y,Z,TV)
      CALL OVRLAP(N,ATOM,X,Y,Z,TV,S,T,NDIM)
      CALL OVRLAP2(N,ATOM,X,Y,Z,TV,SF)
      CALL POTNTL(N,ATOM,SF,V,NDIM)
      READ (1,*) NVAL
      IF (NVAL.NE.0) CALL OUTSET(ATOM,N,ATOM2,ORB,NDIM)
C
      DO 10 I=1,11
      CALL FOCK(I,NDIM,S,T,V,SB,F)
      CALL EIGEN(NDIM,SB,F,C,E)
      CALL OUTPUT(NVAL,I,ATOM2,ORB,NDIM,E,C)
 10   CONTINUE
      STOP
      END
C
      SUBROUTINE INPUT(N,ATOM,X,Y,Z,TV)
C
C      THIS SUBROUTINE READS THE INFORMATION NECESSARY TO DO THE VEH
C      CALCULATION, WHICH IS MAINLY THE COORDINATES OF EACH ATOM IN THE
C      UNIT CELL AND THE SIZE AND ORIENTATION OF THE UNIT CELL (DEFINED
```

```
C       BY THE TRANSLATION VECTOR, TV). IT ALSO STARTS WRITING THE
C       OUTPUT FILE.
C
      IMPLICIT REAL*8 (A-H,O-Z)
      CHARACTER*60 TITLE,STITLE
      CHARACTER*2 ATOM(40)
      DIMENSION TV(3)
      DIMENSION X(40),Y(40),Z(40)
C
      READ(1,9) TITLE
      READ(1,9) STITLE
 9    FORMAT(A60)
C
      WRITE(2,11)
      WRITE(2,12) TITLE
      WRITE(2,12) STITLE
 11   FORMAT(' VALENCE EFFECTIVE HAMILTONIAN CALCULATION FOR POLYMERS'/)
 12   FORMAT(1X,A60)
C
      READ(1,*)N
      READ(1,10) (ATOM(I),X(I),Y(I),Z(I),I=1,N)
      READ(1,19) TV(1),TV(2),TV(3)
 10   FORMAT(A2,3F9.5)
 19   FORMAT(3F9.5)
C
      WRITE(2,13) N
      WRITE(2,14)
      WRITE(2,15) (ATOM(I),X(I),Y(I),Z(I),I=1,N)
      WRITE(2,16) TV(1),TV(2),TV(3)
 13   FORMAT(/ ' NUMBER OF ATOMS PER UNIT CELL =',I4)
 14   FORMAT(/' ATOM      X-COORDINATE      Y-COORDINATE      ',
     *'Z-COORDINATE'/)
 15   FORMAT(2X,A2,8X,F9.5,9X,F9.5,9X,F9.5)
 16   FORMAT(/' TRANSLATION VECTOR '/12X,F9.5,9X,F9.5,9X,F9.5)
C
C       CHANGE INTO ATOMIC UNITS
C
      DO 20 I=1,N
      X(I)=X(I)/0.52917706
      Y(I)=Y(I)/0.52917706
 20   Z(I)=Z(I)/0.52917706
      DO 21 I=1,3
 21   TV(I)=TV(I)/0.52917706
C
      RETURN
      END
C
      SUBROUTINE OVRLAP(N,ATOM,X,Y,Z,TV,S,T,NDIM)
C
C       CONSTRUCTS THE OVERLAP AND KINETIC ENERGY MATRIX ELEMENTS
C       BETWEEN ATOMIC ORBITALS.
C
      IMPLICIT REAL*8 (A-H,O-Z)
```

```
      CHARACTER*2 ATOM(40)
      DIMENSION TV(3)
      DIMENSION X(40),Y(40),Z(40)
      DIMENSION S(5,100,100),T(5,100,100)
      DIMENSION ALPHA0(3),ALPHAJ(3),COF0(3),COFJ(3)
      PI=3.141592654
C
C      LOOP OVER J: J IS AN INDEX INDICATING NEIGHBORING UNIT CELLS
C      I.E. J=1 MEANS THE SAME UNIT CELL, J=2 INDICATES NEAREST NEIGHBORS
C      ETC. UP TO FOURTH NEIGHBOR (J=5) INTERACTIONS ARE CALCULATED.
C
      DO 1000 J=1,5
      INDEX=1
C
C      LOOP OVER ATOMS IN REFERENCE UNIT CELL. THIS WILL BE THE ROWS.
C
      DO 900 IROW=1,N
C
C      LOOP OVER ORBITALS IN EACH ATOM. ASSIGN PARAMETERS TO EACH ATOM.
C
      DO 800 K=1,4
      IF (ATOM(IROW).NE.'H ') GO TO 20
      ALPHA0(1)=3.04944
      ALPHA0(2)=0.555460
      ALPHA0(3)=0.150330
      COF0(1)=0.154329
      COF0(2)=0.535328
      COF0(3)=0.444635
      GO TO 100
 20   IF ((ATOM(IROW).NE.'C ').AND.(ATOM(IROW).NE.'CN').AND.
     *(ATOM(IROW).NE.'CO').AND.(ATOM(IROW).NE.'CS'))  GO TO 22
      ALPHA0(1)=3.07964
      ALPHA0(2)=0.715642
      ALPHA0(3)=0.232749
      IF (K.NE.1) GO TO 21
      COF0(1)=-0.0999672
      COF0(2)=0.399513
      COF0(3)=0.700115
      GO TO 100
 21   COF0(1)=0.155916
      COF0(2)=0.607694
      COF0(3)=0.391957
      GO TO 100
 22   IF (ATOM(IROW).NE.'S ') GO TO 24
      ALPHA0(1)=1.83605
      ALPHA0(2)=0.512254
      ALPHA0(3)=0.200493
      IF (K.NE.1) GO TO 23
      COF0(1)=-0.219620
      COF0(2)=0.225565
      COF0(3)=0.900398
      GO TO 100
 23   COF0(1)=0.0105876
```

```
      COF0(2)=0.595167
      COF0(3)=0.462001
      GO TO 100
 24   IF (ATOM(IROW).NE.'N ') GO TO 26
      ALPHA0(1)=3.78046
      ALPHA0(2)=0.878495
      ALPHA0(3)=0.285715
      IF (K.NE.1) GO TO 25
      COF0(1)=-0.0999672
      COF0(2)=0.399513
      COF0(3)=0.700115
      GO TO 100
 25   COF0(1)=0.155916
      COF0(2)=0.607694
      COF0(3)=0.391957
      GO TO 100
 26   IF (ATOM(IROW).NE.'O ') GO TO 28
      ALPHA0(1)=5.03315
      ALPHA0(2)=1.16959
      ALPHA0(3)=0.380389
      IF (K.NE.1) GO TO 27
      COF0(1)=-0.0999672
      COF0(2)=0.399513
      COF0(3)=0.700115
      GO TO 100
 27   COF0(1)=0.155916
      COF0(2)=0.607694
      COF0(3)=0.391957
      GO TO 100
 28   WRITE(2,29) IROW
 29   FORMAT(/ ' NO PARAMETERS AVAILABLE FOR ATOM NO.', I4/
     *' CALCULATION TERMINATED')
      STOP
C
 100  CONTINUE
C
C      LOOP OVER ATOMS IN THE JTH UNIT CELL. THIS WILL BE THE COLUMNS.
C
      JNDEX=1
      DO 700 ICOL=1,N
C
C      CALCULATE DISTANCE BETWEEN ATOMS IROW AND ICOL. THE TWO MAY BE
C      IN DIFFERENT UNIT CELLS.
C
      DELX=(J-1)*TV(1)+X(ICOL)-X(IROW)
      DELY=(J-1)*TV(2)+Y(ICOL)-Y(IROW)
      DELZ=(J-1)*TV(3)+Z(ICOL)-Z(IROW)
      DIST=DSQRT(DELX**2+DELY**2+DELZ**2)
C
C      LOOP OVER ORBITALS.
C
      DO 600 L=1,4
C
```

```
      IF (ATOM(ICOL).NE.'H ') GO TO 120
      ALPHAJ(1)=3.04944
      ALPHAJ(2)=0.555460
      ALPHAJ(3)=0.150330
      COFJ(1)=0.154329
      COFJ(2)=0.535328
      COFJ(3)=0.444635
      GO TO 200
120   IF ((ATOM(ICOL).NE.'C ').AND.(ATOM(ICOL).NE.'CN').AND.
     *(ATOM(ICOL).NE.'CO').AND.(ATOM(ICOL).NE.'CS'))  GO TO 122
      ALPHAJ(1)=3.07964
      ALPHAJ(2)=0.715642
      ALPHAJ(3)=0.232749
      IF (L.NE.1) GO TO 121
      COFJ(1)=-0.0999672
      COFJ(2)=0.399513
      COFJ(3)=0.700115
      GO TO 200
121   COFJ(1)=0.155916
      COFJ(2)=0.607694
      COFJ(3)=0.391957
      GO TO 200
122   IF (ATOM(ICOL).NE.'S ') GO TO 124
      ALPHAJ(1)=1.83605
      ALPHAJ(2)=0.512254
      ALPHAJ(3)=0.200493
      IF (L.NE.1) GO TO 123
      COFJ(1)=-0.219620
      COFJ(2)=0.225565
      COFJ(3)=0.900398
      GO TO 200
123   COFJ(1)=0.0105876
      COFJ(2)=0.595167
      COFJ(3)=0.462001
      GO TO 200
124   IF (ATOM(ICOL).NE.'N ') GO TO 126
      ALPHAJ(1)=3.78046
      ALPHAJ(2)=0.878495
      ALPHAJ(3)=0.285715
      IF (L.NE.1) GO TO 125
      COFJ(1)=-0.0999672
      COFJ(2)=0.399513
      COFJ(3)=0.700115
      GO TO 200
125   COFJ(1)=0.155916
      COFJ(2)=0.607694
      COFJ(3)=0.391957
      GO TO 200
126   IF (ATOM(ICOL).NE.'O ') GO TO 128
      ALPHAJ(1)=5.03315
      ALPHAJ(2)=1.16959
      ALPHAJ(3)=0.380389
      IF (L.NE.1) GO TO 127
```

```
      COFJ(1)=-0.0999672
      COFJ(2)=0.399513
      COFJ(3)=0.700115
      GO TO 200
  127 COFJ(1)=0.155916
      COFJ(2)=0.607694
      COFJ(3)=0.391957
      GO TO 200
  128  WRITE(2,29) ICOL
      STOP
C
  200 CONTINUE
C
C      CALCULATE MATRIX ELEMENTS (FINALLY!)
C
      S(J,INDEX,JNDEX)=0.0
      T(J,INDEX,JNDEX)=0.0
C
      DO 500 MM=1,3
      DO 500 MN=1,3
C
      RECUR=(ALPHA0(MM)*ALPHAJ(MN))/(ALPHA0(MM)+ALPHAJ(MN))
      CONST=(PI/(ALPHA0(MM)+ALPHAJ(MN)))**1.5*DEXP(-RECUR*DIST**2)
      IF (K.NE.1) GO TO 250
C
C      S AND S ORBITALS
C
      IF (L.NE.1) GO TO 210
      FACTOR=(4*ALPHA0(MM)*ALPHAJ(MN)/PI**2)**0.75
      SINK=FACTOR*CONST
      TINK=(3*RECUR-2*RECUR**2*DIST**2)*SINK
      GO TO 490
C
C      S AND PX ORBITALS
C
  210 IF (L.NE.2) GO TO 220
      FACTOR=2*DSQRT(ALPHAJ(MN))*(4*ALPHA0(MM)*ALPHAJ(MN)/PI**2)**0.75
      SINK=-(RECUR/ALPHAJ(MN))*DELX*FACTOR*CONST
      TINK=(5*RECUR-2*RECUR**2*DIST**2)*SINK
      GO TO 490
C
C      S AND PY ORBITALS
C
  220 IF (L.NE.3) GO TO 230
      FACTOR=2*DSQRT(ALPHAJ(MN))*(4*ALPHA0(MM)*ALPHAJ(MN)/PI**2)**0.75
      SINK=-(RECUR/ALPHAJ(MN))*DELY*FACTOR*CONST
      TINK=(5*RECUR-2*RECUR**2*DIST**2)*SINK
      GO TO 490
C
C      S AND PZ ORBITALS
C
  230 IF (L.NE.4) GO TO 240
      FACTOR=2*DSQRT(ALPHAJ(MN))*(4*ALPHA0(MM)*ALPHAJ(MN)/PI**2)**0.75
```

```
      SINK=-(RECUR/ALPHAJ(MN))*DELZ*FACTOR*CONST
      TINK=(5*RECUR-2*RECUR**2*DIST**2)*SINK
      GO TO 490
C
 240  WRITE(2,241)
 241  FORMAT(' THIS MESSAGE IS NOT SUPPOSED TO APPEAR AT ANY TIME ')
      GO TO 490
C
 250  IF (K.NE.2) GO TO 300
C
C      PX AND S ORBITALS
C
      IF (L.NE.1) GO TO 260
      FACTOR=2*DSQRT(ALPHA0(MM))*(4*ALPHA0(MM)*ALPHAJ(MN)/PI**2)**0.75
      SINK=(RECUR/ALPHA0(MM))*DELX*FACTOR*CONST
      TINK=(5*RECUR-2*RECUR**2*DIST**2)*SINK
      GO TO 490
C
C      PX AND PX ORBITALS
C
 260  IF (L.NE.2) GO TO 270
      FACTOR=4*DSQRT(ALPHA0(MM)*ALPHAJ(MN))*(4*ALPHA0(MM)*ALPHAJ(MN)/
     &PI**2)**0.75
      SINK=FACTOR*CONST*(-RECUR*DELX**2/(ALPHA0(MM)+
     &ALPHAJ(MN))+0.5/(ALPHA0(MM)+ALPHAJ(MN)))
      TINK=(5*RECUR-2*RECUR**2*DIST**2)*SINK-
     &2*RECUR**2*DELX**2*CONST*FACTOR/(ALPHA0(MM)+ALPHAJ(MN))
      GO TO 490
C
C      PX AND PY ORBITALS
C
 270  IF (L.NE.3) GO TO 280
      FACTOR=4*DSQRT(ALPHA0(MM)*ALPHAJ(MN))*(4*ALPHA0(MM)*ALPHAJ(MN)/
     &PI**2)**0.75
      SINK=-RECUR*DELX*DELY/(ALPHA0(MM)+ALPHAJ(MN))*
     &FACTOR*CONST
      TINK=(7*RECUR-2*RECUR**2*DIST**2)*SINK
      GO TO 490
C
C      PX AND PZ ORBITALS
C
 280  IF (L.NE.4) GO TO 240
      FACTOR=4*DSQRT(ALPHA0(MM)*ALPHAJ(MN))*(4*ALPHA0(MM)*ALPHAJ(MN)/
     &PI**2)**0.75
      SINK=-RECUR*DELX*DELZ/(ALPHA0(MM)+ALPHAJ(MN))*
     &FACTOR*CONST
      TINK=(7*RECUR-2*RECUR**2*DIST**2)*SINK
      GO TO 490
C
 300  IF (K.NE.3) GO TO 350
C
C      PY AND S ORBITALS
C
```

```
      IF (L.NE.1) GO TO 310
      FACTOR=2*DSQRT(ALPHA0(MM))*(4*ALPHA0(MM)*ALPHAJ(MN)/PI**2)**0.75
      SINK=(RECUR/ALPHA0(MM))*DELY*FACTOR*CONST
      TINK=(5*RECUR-2*RECUR**2*DIST**2)*SINK
      GO TO 490
C
C       PY AND PX ORBITALS
C
 310  IF (L.NE.2) GO TO 320
      FACTOR=4*DSQRT(ALPHA0(MM)*ALPHAJ(MN))*(4*ALPHA0(MM)*ALPHAJ(MN)/
     &PI**2)**0.75
      SINK=-RECUR*DELY*DELX/(ALPHA0(MM)+ALPHAJ(MN))*
     &FACTOR*CONST
      TINK=(7*RECUR-2*RECUR**2*DIST**2)*SINK
      GO TO 490
C
C       PY AND PY ORBITALS
C
 320  IF (L.NE.3) GO TO 330
      FACTOR=4*DSQRT(ALPHA0(MM)*ALPHAJ(MN))*(4*ALPHA0(MM)*ALPHAJ(MN)/
     &PI**2)**0.75
      SINK=FACTOR*CONST*(-RECUR*DELY**2/(ALPHA0(MM)+
     &ALPHAJ(MN))+0.5/(ALPHA0(MM)+ALPHAJ(MN)))
      TINK=(5*RECUR-2*RECUR**2*DIST**2)*SINK-
     &2*RECUR**2*DELY**2*CONST*FACTOR/(ALPHA0(MM)+ALPHAJ(MN))
      GO TO 490
C
C       PY AND PZ ORBITALS
C
 330  IF (L.NE.4) GO TO 240
      FACTOR=4*DSQRT(ALPHA0(MM)*ALPHAJ(MN))*(4*ALPHA0(MM)*ALPHAJ(MN)/
     &PI**2)**0.75
      SINK=-RECUR*DELY*DELZ/(ALPHA0(MM)+ALPHAJ(MN))*
     &FACTOR*CONST
      TINK=(7*RECUR-2*RECUR**2*DIST**2)*SINK
      GO TO 490
C
 350  IF (K.NE.4) GO TO 240
C
C       PZ AND S ORBITALS
C
      IF (L.NE.1) GO TO 360
      FACTOR=2*DSQRT(ALPHA0(MM))*(4*ALPHA0(MM)*ALPHAJ(MN)/PI**2)**0.75
      SINK=(RECUR/ALPHA0(MM))*DELZ*FACTOR*CONST
      TINK=(5*RECUR-2*RECUR**2*DIST**2)*SINK
      GO TO 490
C
C       PZ AND PX ORBITALS
C
 360  IF (L.NE.2) GO TO 370
      FACTOR=4*DSQRT(ALPHA0(MM)*ALPHAJ(MN))*(4*ALPHA0(MM)*ALPHAJ(MN)/
     &PI**2)**0.75
      SINK=-RECUR*DELZ*DELX/(ALPHA0(MM)+ALPHAJ(MN))*
```

```
     &FACTOR*CONST
      TINK=(7*RECUR-2*RECUR**2*DIST**2)*SINK
      GO TO 490
C
C       PZ AND PY ORBITALS
C
 370  IF (L.NE.3) GO TO 380
      FACTOR=4*DSQRT(ALPHA0(MM)*ALPHAJ(MN))*(4*ALPHA0(MM)*ALPHAJ(MN)/
     &PI**2)**0.75
      SINK=-RECUR*DELZ*DELY/(ALPHA0(MM)+ALPHAJ(MN))*
     &FACTOR*CONST
      TINK=(7*RECUR-2*RECUR**2*DIST**2)*SINK
      GO TO 490
C
C       PZ AND PZ ORBITALS
C
 380  IF (L.NE.4) GO TO 240
      FACTOR=4*DSQRT(ALPHA0(MM)*ALPHAJ(MN))*(4*ALPHA0(MM)*ALPHAJ(MN)/
     &PI**2)**0.75
      SINK=FACTOR*CONST*(-RECUR*DELZ**2/(ALPHA0(MM)+
     &ALPHAJ(MN))+0.5/(ALPHA0(MM)+ALPHAJ(MN)))
      TINK=(5*RECUR-2*RECUR**2*DIST**2)*SINK-
     &2*RECUR**2*DELZ**2*CONST*FACTOR/(ALPHA0(MM)+ALPHAJ(MN))
      GO TO 490
C
 490  CONTINUE
C
      SINK=COF0(MM)*COFJ(MN)*SINK
      TINK=COF0(MM)*COFJ(MN)*TINK
      S(J,INDEX,JNDEX)=S(J,INDEX,JNDEX)+SINK
      T(J,INDEX,JNDEX)=T(J,INDEX,JNDEX)+TINK
C
 500  CONTINUE
      JNDEX=JNDEX+1
C
C       IF ATOM IS HYDROGEN, BREAK OUT OF L-LOOP SINCE THERE ARE NO
C       P ORBITALS
C
      IF (ATOM(ICOL).EQ.'H ') GO TO 601
 600  CONTINUE
 601  CONTINUE
 700  CONTINUE
C
C       END OF LOOPS OVER COLUMNS. NOW FOR ROWS.
C
      INDEX=INDEX+1

C
C       AGAIN, BREAK OUT OF K-LOOP IF ATOM IS HYDROGEN
C
      IF (ATOM(IROW).EQ.'H ') GO TO 801
 800  CONTINUE
 801  CONTINUE
```

```
 900  CONTINUE
 1000 CONTINUE
      NDIM=INDEX-1
C
      RETURN
      END
C
      SUBROUTINE OVRLAP2(N,ATOM,X,Y,Z,TV,S)
C
C      CONSTRUCTS A FAKE OVERLAP MATRIX FOR USE IN POTENTIAL ENERGY
C      CALCULATION.
C
      IMPLICIT REAL*8 (A-H,O-Z)
      CHARACTER*2 ATOM(40)
      DIMENSION TV(3)
      DIMENSION X(40),Y(40),Z(40)
      DIMENSION S(9,100,200)
      DIMENSION ALPHA0(3),ALPHAJ(2),COF0(3)
      PI=3.141592654
C
      DO 1000 J=1,9
      INDEX=1
C
C      LOOP OVER ATOMS IN REFERENCE UNIT CELL. THIS WILL BE THE ROWS.
C
      DO 900 IROW=1,N
C
C      LOOP OVER ORBITALS IN EACH ATOM. ASSIGN PARAMETERS TO EACH ATOM.
C
      DO 800 K=1,4
      IF (ATOM(IROW).NE.'H ') GO TO 20
      ALPHA0(1)=3.04944
      ALPHA0(2)=0.555460
      ALPHA0(3)=0.150330
      COF0(1)=0.154329
      COF0(2)=0.535328
      COF0(3)=0.444625
      GO TO 100
 20   IF ((ATOM(IROW).NE.'C ').AND.(ATOM(IROW).NE.'CN').AND.
     *(ATOM(IROW).NE.'CO').AND.(ATOM(IROW).NE.'CS'))  GO TO 22
      ALPHA0(1)=3.07964
      ALPHA0(2)=0.715642
      ALPHA0(3)=0.232749
      IF (K.NE.1) GO TO 21
      COF0(1)=-0.0999672
      COF0(2)=0.399513
      COF0(3)=0.700115
      GO TO 100
 21   COF0(1)=0.155916
      COF0(2)=0.607684
      COF0(3)=0.391957
      GO TO 100
 22   IF (ATOM(IROW).NE.'S ') GO TO 24
```

```
      ALPHA0(1)=1.83605
      ALPHA0(2)=0.512254
      ALPHA0(3)=0.200493
      IF (K.NE.1) GO TO 23
      COF0(1)=-0.219620
      COF0(2)=0.225595
      COF0(3)=0.900398
      GO TO 100
 23   COF0(1)=0.0105876
      COF0(2)=0.595167
      COF0(3)=0.462001
      GO TO 100
 24   IF (ATOM(IROW).NE.'N ') GO TO 26
      ALPHA0(1)=3.78046
      ALPHA0(2)=0.878495
      ALPHA0(3)=0.285715
      IF (K.NE.1) GO TO 25
      COF0(1)=-0.0999672
      COF0(2)=0.399513
      COF0(3)=0.700115
      GO TO 100
 25   COF0(1)=0.155916
      COF0(2)=0.607684
      COF0(3)=0.391957
      GO TO 100
 26   IF (ATOM(IROW).NE.'O ') GO TO 28
      ALPHA0(1)=5.03315
      ALPHA0(2)=1.16959
      ALPHA0(3)=0.380389
      IF (K.NE.1) GO TO 27
      COF0(1)=-0.0999672
      COF0(2)=0.399513
      COF0(3)=0.700115
      GO TO 100
 27   COF0(1)=0.155916
      COF0(2)=0.607684
      COF0(3)=0.391957
      GO TO 100
 28   WRITE(2,29) IROW
 29   FORMAT(/ ' NO PARAMETERS AVAILABLE FOR ATOM NO.', I4/
     *' CALCULATION TERMINATED')
      STOP
C
 100  CONTINUE
C
C      LOOP OVER ATOMS IN THE JTH UNIT CELL. THIS WILL BE THE COLUMNS.
C
      JNDEX=1
      DO 700 ICOL=1,N
C
C      CALCULATE DISTANCE BETWEEN ATOMS IROW AND ICOL. THE TWO MAY BE
C      IN DIFFERENT UNIT CELLS.
C
```

```
      DELX=(J-5)*TV(1)+X(ICOL)-X(IROW)
      DELY=(J-5)*TV(2)+Y(ICOL)-Y(IROW)
      DELZ=(J-5)*TV(3)+Z(ICOL)-Z(IROW)
      DIST=DSQRT(DELX**2+DELY**2+DELZ**2)
C
C       LOOP OVER ORBITALS.
C
      DO 600 L=1,4
      IF (ATOM(ICOL).NE.'H ') GO TO 120
      ALPHAJ(1)=5.00
      ALPHAJ(2)=0.49
      GO TO 200
 120  IF ((ATOM(ICOL).NE.'C ').AND.(ATOM(ICOL).NE.'CN').AND.
     *(ATOM(ICOL).NE.'CO').AND.(ATOM(ICOL).NE.'CS'))  GO TO 122
      IF (L.NE.1) GO TO 121
      ALPHAJ(1)=3.63
      ALPHAJ(2)=0.33
      GO TO 200
 121  ALPHAJ(1)=6.50
      ALPHAJ(2)=0.52
      GO TO 200
 122  IF (ATOM(ICOL).NE.'S ') GO TO 124
      IF (L.NE.1) GO TO 123
      ALPHAJ(1)=1.00
      ALPHAJ(2)=0.30
      GO TO 200
 123  ALPHAJ(1)=0.90
      ALPHAJ(2)=0.20
      GO TO 200
 124  IF (ATOM(ICOL).NE.'N ') GO TO 126
      IF (L.NE.1) GO TO 125
      ALPHAJ(1)=1.50
      ALPHAJ(2)=0.50
      GO TO 200
 125  ALPHAJ(1)=3.00
      ALPHAJ(2)=0.35
      GO TO 200
 126  IF (ATOM(ICOL).NE.'O ') GO TO 128
      IF (L.NE.1) GO TO 127
      ALPHAJ(1)=5.00
      ALPHAJ(2)=0.50
      GO TO 200
 127  ALPHAJ(1)=2.89
      ALPHAJ(2)=0.065
      GO TO 200
 128  WRITE(2,29) ICOL
      STOP
C
 200  CONTINUE
C
C       LOOP OVER GAUSSIANS.
C
      DO 500 MN=1,2
```

```
C
C       CALCULATE MATRIX ELEMENTS (FINALLY!)
C
        S(J,INDEX,JNDEX)=0.0
        DO 495 MM=1,3
C
        RECUR=(ALPHA0(MM)*ALPHAJ(MN))/(ALPHA0(MM)+ALPHAJ(MN))
        CONST=(PI/(ALPHA0(MM)+ALPHAJ(MN)))**1.5*DEXP(-RECUR*DIST**2)
        IF (K.NE.1) GO TO 250
C
C       S AND S ORBITALS
C
        IF (L.NE.1) GO TO 210
        FACTOR=(4*ALPHA0(MM)*ALPHAJ(MN)/PI**2)**0.75
        SINK=FACTOR*CONST
        GO TO 490
C
C       S AND PX ORBITALS
C
 210    IF (L.NE.2) GO TO 220
        FACTOR=2*DSQRT(ALPHAJ(MN))*(4*ALPHA0(MM)*ALPHAJ(MN)/PI**2)**0.75
        SINK=-(RECUR/ALPHAJ(MN))*DELX*FACTOR*CONST
        GO TO 490
C
C       S AND PY ORBITALS
C
 220    IF (L.NE.3) GO TO 230
        FACTOR=2*DSQRT(ALPHAJ(MN))*(4*ALPHA0(MM)*ALPHAJ(MN)/PI**2)**0.75
        SINK=-(RECUR/ALPHAJ(MN))*DELY*FACTOR*CONST
        GO TO 490
C
C       S AND PZ ORBITALS
C
 230    IF (L.NE.4) GO TO 240
        FACTOR=2*DSQRT(ALPHAJ(MN))*(4*ALPHA0(MM)*ALPHAJ(MN)/PI**2)**0.75
        SINK=-(RECUR/ALPHAJ(MN))*DELZ*FACTOR*CONST
        GO TO 490
C
 240    WRITE(2,241)
 241    FORMAT(' THIS MESSAGE IS NOT SUPPOSED TO APPEAR AT ANY TIME ')
        GO TO 490
C
 250    IF (K.NE.2) GO TO 300
C
C       PX AND S ORBITALS
C
        IF (L.NE.1) GO TO 260
        FACTOR=2*DSQRT(ALPHA0(MM))*(4*ALPHA0(MM)*ALPHAJ(MN)/PI**2)**0.75
        SINK=(RECUR/ALPHA0(MM))*DELX*FACTOR*CONST
        GO TO 490
C
C       PX AND PX ORBITALS
C
```

```
 260  IF (L.NE.2) GO TO 270
      FACTOR=4*DSQRT(ALPHA0(MM)*ALPHAJ(MN))*(4*ALPHA0(MM)*ALPHAJ(MN)/
     &PI**2)**0.75
      SINK=FACTOR*CONST*(-RECUR*DELX**2/(ALPHA0(MM)+
     &ALPHAJ(MN))+0.5/(ALPHA0(MM)+ALPHAJ(MN)))
      GO TO 490
C
C       PX AND PY ORBITALS
C
 270  IF (L.NE.3) GO TO 280
      FACTOR=4*DSQRT(ALPHA0(MM)*ALPHAJ(MN))*(4*ALPHA0(MM)*ALPHAJ(MN)/
     &PI**2)**0.75
      SINK=-RECUR*DELX*DELY/(ALPHA0(MM)+ALPHAJ(MN))*
     &FACTOR*CONST
      GO TO 490
C
C       PX AND PZ ORBITALS
C
 280  IF (L.NE.4) GO TO 240
      FACTOR=4*DSQRT(ALPHA0(MM)*ALPHAJ(MN))*(4*ALPHA0(MM)*ALPHAJ(MN)/
     &PI**2)**0.75
      SINK=-RECUR*DELX*DELZ/(ALPHA0(MM)+ALPHAJ(MN))*
     &FACTOR*CONST
      GO TO 490
C
 300  IF (K.NE.3) GO TO 350
C
C       PY AND S ORBITALS
C
      IF (L.NE.1) GO TO 310
      FACTOR=2*DSQRT(ALPHA0(MM))*(4*ALPHA0(MM)*ALPHAJ(MN)/PI**2)**0.75
      SINK=(RECUR/ALPHA0(MM))*DELY*FACTOR*CONST
      GO TO 490
C
C       PY AND PX ORBITALS
C
 310  IF (L.NE.2) GO TO 320
      FACTOR=4*DSQRT(ALPHA0(MM)*ALPHAJ(MN))*(4*ALPHA0(MM)*ALPHAJ(MN)/
     &PI**2)**0.75
      SINK=-RECUR*DELY*DELX/(ALPHA0(MM)+ALPHAJ(MN))*
     &FACTOR*CONST
      GO TO 490
C
C       PY AND PY ORBITALS
C
 320  IF (L.NE.3) GO TO 330
      FACTOR=4*DSQRT(ALPHA0(MM)*ALPHAJ(MN))*(4*ALPHA0(MM)*ALPHAJ(MN)/
     &PI**2)**0.75
      SINK=FACTOR*CONST*(-RECUR*DELY**2/(ALPHA0(MM)+
     &ALPHAJ(MN))+0.5/(ALPHA0(MM)+ALPHAJ(MN)))
      GO TO 490
C
C       PY AND PZ ORBITALS
```

```
C
 330  IF (L.NE.4) GO TO 240
      FACTOR=4*DSQRT(ALPHA0(MM)*ALPHAJ(MN))*(4*ALPHA0(MM)*ALPHAJ(MN)/
     &PI**2)**0.75
      SINK=-RECUR*DELY*DELZ/(ALPHA0(MM)+ALPHAJ(MN))*
     &FACTOR*CONST
      GO TO 490
C
 350  IF (K.NE.4) GO TO 240
C
C      PZ AND S ORBITALS
C
      IF (L.NE.1) GO TO 360
      FACTOR=2*DSQRT(ALPHA0(MM))*(4*ALPHA0(MM)*ALPHAJ(MN)/PI**2)**0.75
      SINK=(RECUR/ALPHA0(MM))*DELZ*FACTOR*CONST
      GO TO 490
C
C      PZ AND PX ORBITALS
C
 360  IF (L.NE.2) GO TO 370
      FACTOR=4*DSQRT(ALPHA0(MM)*ALPHAJ(MN))*(4*ALPHA0(MM)*ALPHAJ(MN)/
     &PI**2)**0.75
      SINK=-RECUR*DELZ*DELX/(ALPHA0(MM)+ALPHAJ(MN))*
     &FACTOR*CONST
      GO TO 490
C
C      PZ AND PY ORBITALS
C
 370  IF (L.NE.3) GO TO 380
      FACTOR=4*DSQRT(ALPHA0(MM)*ALPHAJ(MN))*(4*ALPHA0(MM)*ALPHAJ(MN)/
     &PI**2)**0.75
      SINK=-RECUR*DELZ*DELY/(ALPHA0(MM)+ALPHAJ(MN))*
     &FACTOR*CONST
      GO TO 490
C
C      PZ AND PZ ORBITALS
C
 380  IF (L.NE.4) GO TO 240
      FACTOR=4*DSQRT(ALPHA0(MM)*ALPHAJ(MN))*(4*ALPHA0(MM)*ALPHAJ(MN)/
     &PI**2)**0.75
      SINK=FACTOR*CONST*(-RECUR*DELZ**2/(ALPHA0(MM)+
     &ALPHAJ(MN))+0.5/(ALPHA0(MM)+ALPHAJ(MN)))
      GO TO 490
C
 490  CONTINUE
C
      SINK=COF0(MM)*SINK
      S(J,INDEX,JNDEX)=S(J,INDEX,JNDEX)+SINK
C
 495  CONTINUE
      JNDEX=JNDEX+1
 500  CONTINUE
C
```

```
C       IF ATOM IS HYDROGEN, BREAK OUT OF L-LOOP SINCE THERE ARE NO
C       P ORBITALS
C
        IF (ATOM(ICOL).EQ.'H ') GO TO 601
  600   CONTINUE
  601   CONTINUE
  700   CONTINUE
C
C       END OF LOOPS OVER COLUMNS. NOW FOR ROWS.
C
        INDEX=INDEX+1

C
C       AGAIN, BREAK OUT OF K-LOOP IF ATOM IS HYDROGEN
C
        IF (ATOM(IROW).EQ.'H ') GO TO 801
  800   CONTINUE
  801   CONTINUE
  900   CONTINUE
 1000   CONTINUE
C
        RETURN
        END
C
        SUBROUTINE POTNTL(N,ATOM,S,V,NDIM)
C
C       CONSTRUCTS THE POTENTIAL ENERGY MATRIX ELEMENTS BETWEEN ATOMIC
C       ORBITALS.
C
        IMPLICIT REAL*8 (A-H,O-Z)
        CHARACTER*2 ATOM(40)
        DIMENSION S(9,100,200),V(5,100,100)
C
C       LOOP OVER J: J IS AN INDEX INDICATING NEIGHBORING UNIT CELLS
C       I.E. J=1 MEANS THE SAME UNIT CELL, J=2 INDICATES NEAREST NEIGHBORS
C       ETC. UP TO FOURTH NEIGHBOR (J=5) INTERACTIONS ARE CALCULATED.
C
        DO 1000 J=1,5
        JMAX=10-J
C
C       LOOP OVER ROWS
C
        DO 995 IROW=1,NDIM
C
C       LOOP OVER COLUMNS
C
        DO 990 ICOL=1,NDIM
        V(J,IROW,ICOL)=0.0
C
C       SUM OVER UNIT CELLS: HOW MANY NEIGHBORS DEPENDS ON J
C
        DO 900 JJ=1,JMAX
        INDEX=1
```

```
C
C       SUM OVER ATOMS IN UNIT CELL
C
      DO 800 KK=1,N
C
C       SUM OVER ORBITALS OF EACH ATOM
C
      DO 700 LL=1,4
C
C       ASSIGN PARAMETERS
C
      IF (ATOM(KK).NE.'H ') GO TO 100
      C11=-4.696091
      C22=-0.500281
      C12=0.646198
      GO TO 200
  100 IF (ATOM(KK).NE.'C ') GO TO 110
      IF (LL.NE.1) GO TO 105
      C11=-10.075111
      C22=-1.177806
      C12=2.076910
      GO TO 200
  105 C11=-11.468190
      C22=-0.442640
      C12=-0.185204
      GO TO 200
  110 IF (ATOM(KK).NE.'CN') GO TO 120
      IF (LL.NE.1) GO TO 115
      C11=-0.486
      C22=0.222
      C12=-1.710
      GO TO 200
  115 C11=-1.637
      C22=0.244
      C12=-2.834
      GO TO 200
  120 IF (ATOM(KK).NE.'CO') GO TO 130
      IF (LL.NE.1) GO TO 125
      C11=-5.347128
      C22=-0.224388
      C12=-0.212415
      GO TO 200
  125 C11=-4.315077
      C22=0.062549
      C12=-2.192423
      GO TO 200
  130 IF (ATOM(KK).NE.'CS') GO TO 140
      IF (LL.NE.1) GO TO 135
      C11=-6.506
      C22=-0.514
      C12=0.354
      GO TO 200
  135 C11=-12.380
```

```
      C22=-0.474
      C12=-0.069
      GO TO 200
  140 IF (ATOM(KK).NE.'N ') GO TO 150
      IF (LL.NE.1) GO TO 145
      C11=1.520
      C22=0.790
      C12=-2.149
      GO TO 200
  145 C11=-4.789
      C22=0.046
      C12=-0.353
      GO TO 200
  150 IF (ATOM(KK).NE.'O ') GO TO 160
      IF (LL.NE.1) GO TO 155
      C11=-8.559475
      C22=-1.386891
      C12=1.107173
      GO TO 200
  155 C11=-5.364173
      C22=-0.065479
      C12=-0.044582
      GO TO 200
  160 IF (ATOM(KK).NE.'S ') GO TO 170
      IF (LL.NE.1) GO TO 165
      C11=3.683
      C22=1.521
      C12=-3.454
      GO TO 200
  165 C11=-1.899
      C22=-0.047
      C12=-0.017
      GO TO 200
  170 WRITE(2,171) KK
  171 FORMAT (/' NO PARAMETERS FOR ATOM NO.',I4/
     &' CALCULATION TERMINATED')
      STOP
  200 CONTINUE
C
      NDISL=JJ+J-1
      SLEF1=S(NDISL,IROW,INDEX)
      SLEF2=S(NDISL,IROW,INDEX+1)
C
      NDISR=JJ
      SRHT1=S(NDISR,ICOL,INDEX)
      SRHT2=S(NDISR,ICOL,INDEX+1)
C
      V(J,IROW,ICOL)=V(J,IROW,ICOL)+C11*SLEF1*SRHT1+C12*SLEF1*
     &SRHT2+C12*SLEF2*SRHT1+C22*SLEF2*SRHT2
C
      INDEX=INDEX+2
C
C      BAIL OUT OF ORBITAL LOOP IF ATOM IS HYDROGEN
```

```
C
      IF (ATOM(KK).EQ.'H ') GO TO 701
 700  CONTINUE
 701  CONTINUE
 800  CONTINUE
 900  CONTINUE
 990  CONTINUE
 995  CONTINUE
 1000 CONTINUE
      RETURN
      END
C
      SUBROUTINE FOCK(I,NDIM,S,T,V,SB,F)
C
C      CONSTRUCTS OVERLAP AND FOCK MATRICES BETWEEN BLOCH ORBITALS
C      AT THE ITH POINT IN THE BRILLOUIN ZONE, WHERE I=1,...,11;
C      I=1 CORRESPONDS TO K=0, I=11 CORRESPONDS TO K=PI/A
C
      IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION S(5,100,100),T(5,100,100),V(5,100,100)
      COMPLEX*16 SB(100,100),F(100,100)
      PI=3.1415926536
      AK=(I-1)*PI/10.0
C
      DO 600 IROW=1,NDIM
      DO 600 ICOL=1,NDIM
      SB(IROW,ICOL)=(0.0,0.0)
      F(IROW,ICOL)=(0.0,0.0)
      DO 500 N=1,9
      JJ=N-5
      IF (JJ.GE.0) GO TO 300
C
      J=6-N
      SB(IROW,ICOL)=SB(IROW,ICOL)+S(J,ICOL,IROW)*DCOS(JJ*AK)*
     &(1.0,0.0)+S(J,ICOL,IROW)*DSIN(JJ*AK)*(0.0,1.0)
      F(IROW,ICOL)=F(IROW,ICOL)+(T(J,ICOL,IROW)+V(J,ICOL,IROW))
     &*DCOS(JJ*AK)*(1.0,0.0)+(T(J,ICOL,IROW)+V(J,ICOL,IROW))*
     &DSIN(JJ*AK)*(0.0,1.0)
      GO TO 500
C
 300  J=N-4
      SB(IROW,ICOL)=SB(IROW,ICOL)+S(J,IROW,ICOL)*DCOS(JJ*AK)*
     &(1.0,0.0)+S(J,IROW,ICOL)*DSIN(JJ*AK)*(0.0,1.0)
      F(IROW,ICOL)=F(IROW,ICOL)+(T(J,IROW,ICOL)+V(J,IROW,ICOL))
     &*DCOS(JJ*AK)*(1.0,0.0)+(T(J,IROW,ICOL)+V(J,IROW,ICOL))*
     &DSIN(JJ*AK)*(0.0,1.0)
C
 500  CONTINUE
 600  CONTINUE
      RETURN
      END
C
      SUBROUTINE EIGEN(NDIM,SB,F,C,E)
```

```
C
C       SUBROUTINE TO SOLVE THE GENERALIZED EIGENPROBLEM F*C=SB*C*E.
C       IT REDUCES THE GENERALIZED PROBLEM TO TWO ORDINARY EIGENPROBLEMS
C       AND SOLVES THEM USING THE IMSL ROUTINE EIGCH. THEN THE EIGENVALUES
C       AND CORRESPONDING EIGENVECTORS ARE SORTED IN ASCENDING ORDER.
C       TO SAVE STORAGE SPACE THE VARIOUS MATRICES ARE USED OVER AND OVER
C       FOR DIFFERENT PURPOSES; THIS CODE MAY NOT BE EASY TO FOLLOW.
C
      IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION E(100)
      COMPLEX*16 SB(100,100),F(100,100),C(100,100),A(100,100),S(5050)
      DIMENSION WK(10400)
      COMPLEX*16 Q
C
C     DUE TO ROUNDOFF ERRORS SOME SMALL IMAGINARY COMPONENT OF THE
C     DIAGONAL ELEMENTS OF SB AND F (WHICH ARE HERMITIAN) MAY BE
C     FOUND. THE FOLLOWING LOOP GETS RID OF THESE.
C
      DO 1 I=1,NDIM
      SB(I,I)=(SB(I,I)+DCONJG(SB(I,I)))/2.0
 1    CONTINUE
C
      ICNT=1
      DO 5 IROW=1,NDIM
      DO 5 JCOL=1,IROW
      S(ICNT)=SB(IROW,JCOL)
      ICNT=ICNT+1
 5    CONTINUE
C
      CALL EIGCH(S,NDIM,2,E,C,100,WK,IER)
C
      IF (WK(1).LE.100.0) GO TO 10
      WRITE (2,110)
 110  FORMAT(/' ******** WARNING ******** '/' THE DIAGONALIZATION',
     &' PROCEDURE DID NOT PERFORM SATISFACTORILY')
 10   CONTINUE
C
C       NORMALIZE EIGENVECTORS
C
      DO 30 I=1,NDIM
      SUM=0.0
      DO 29 J=1,NDIM
      SUM=SUM+(DREAL(C(J,I)))**2+(DIMAG(C(J,I)))**2
 29   CONTINUE
      SUM=DSQRT(SUM)
      DO 28 J=1,NDIM
      C(J,I)=C(J,I)/SUM
 28   CONTINUE
 30   CONTINUE
C
      DO 20 IROW=1,NDIM
      DO 20 JCOL=1,NDIM
      A(IROW,JCOL)=C(IROW,JCOL)*DSQRT(1.0/E(JCOL))
```

```
  20   SB(IROW,JCOL)=DCONJG(C(JCOL,IROW))*DSQRT(1.0/E(IROW))
C
       DO 21 IROW=1,NDIM
       DO 21 ICOL=1,NDIM
       C(IROW,ICOL)=(0.0,0.0)
       DO 22 I=1,NDIM
 22    C(IROW,ICOL)=C(IROW,ICOL)+F(IROW,I)*A(I,ICOL)
 21    CONTINUE
C
       DO 23 IROW=1,NDIM
       DO 23 ICOL=1,NDIM
       F(IROW,ICOL)=(0.0,0.0)
       DO 24 I=1,NDIM
 24    F(IROW,ICOL)=F(IROW,ICOL)+SB(IROW,I)*C(I,ICOL)
 23    CONTINUE
C
       DO 66 I=1,NDIM
       F(I,I)=(F(I,I)+DCONJG(F(I,I)))/2.0
 66    CONTINUE
C
       ICNT=1
       DO 25 IROW=1,NDIM
       DO 25 JCOL=1,IROW
       S(ICNT)=F(IROW,JCOL)
       ICNT=ICNT+1
 25    CONTINUE
C
       CALL EIGCH(S,NDIM,2,E,SB,100,WK,IER)
C
       IF (WK(1).LE.100.0) GO TO 111
       WRITE (2,110)
 111   CONTINUE
C
       DO 112 IROW=1,NDIM
       DO 112 ICOL=1,NDIM
       C(IROW,ICOL)=(0.0,0.0)
       DO 113 I=1,NDIM
 113   C(IROW,ICOL)=C(IROW,ICOL)+A(IROW,I)*SB(I,ICOL)
 112   CONTINUE
C
C       SORTING ROUTINE
C
       DO 200 I=1,NDIM-1
       K=I
       P=E(I)
       DO 190 J=I+1,NDIM
       IF (E(J).LE.P) THEN
       K=J
       P=E(J)
       ENDIF
 190   CONTINUE
       IF (K.NE.I) THEN
       E(K)=E(I)
```

```
      E(I)=P
      DO 180 J=1,NDIM
      Q=C(J,I)
      C(J,I)=C(J,K)
      C(J,K)=Q
 180  CONTINUE
      ENDIF
 200  CONTINUE
C
C      NORMALIZE EIGENVECTORS
C
      DO 300 I=1,NDIM
      SUM=0.0
      DO 290 J=1,NDIM
      SUM=SUM+(DREAL(C(J,I)))**2+(DIMAG(C(J,I)))**2
 290  CONTINUE
      SUM=DSQRT(SUM)
      DO 295 J=1,NDIM
      C(J,I)=C(J,I)/SUM
 295  CONTINUE
 300  CONTINUE
C
      RETURN
      END
C
      SUBROUTINE OUTSET(ATOM,N,ATOM2,ORB,NDIM)
C
C      DOES SOME ARRAY INITIALIZATION FOR USE WHEN SUBROUTINE
C      OUTPUT IS CALLED LATER
C
      IMPLICIT REAL*8 (A-H,O-Z)
      CHARACTER*2 ATOM(40),ATOM2(100),ORB(100)
C
      DO 10 I=1,NDIM
 10   ATOM2(I)='  '
C
      INDEX=1
      DO 30 K=1,N
      DO 20 L=1,4
      IF (L.EQ.1) ATOM2(INDEX)=ATOM(K)
      IF (L.EQ.1) ORB(INDEX)='S '
      IF (L.EQ.2) ORB(INDEX)='PX'
      IF (L.EQ.3) ORB(INDEX)='PY'
      IF (L.EQ.4) ORB(INDEX)='PZ'
      INDEX=INDEX+1
      IF (ATOM(K).EQ.'H ') GO TO 21
 20   CONTINUE
 21   CONTINUE
 30   CONTINUE
C
      RETURN
      END
C
```

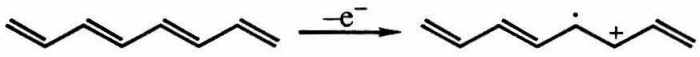
```
      SUBROUTINE OUTPUT(NVAL,KV,ATOM2,ORB,NDIM,E,C)
C
C      WRITES RESULTS IN A REASONABLY UNDERSTANDABLE FORMAT
C
      IMPLICIT REAL*8 (A-H,O-Z)
      COMPLEX*16 C(100,100)
      DIMENSION E(100)
      CHARACTER*2 ATOM(40),ATOM2(100),ORB(100)
C
      KVEC=KV-1
      WRITE (2,100) KVEC
 100  FORMAT (//' K = ',I4,' *PI/10A')
C
      WRITE (2,3)
      WRITE (2,4) (E(I),I=1,NDIM)
      WRITE (3,6) (E(I),I=1,NDIM)
 3    FORMAT (/' EIGENVALUES (A.U.):')
 4    FORMAT (10F7.3)
 6    FORMAT (18F7.3)
      IF (NVAL.EQ.0) GO TO 1000
      WRITE (2,5)
 5    FORMAT (/' EIGENVECTORS:')
C
      IST=1
 101  WRITE (2,110) (E(I),I=IST,MIN(IST+4,NVAL))
      DO 120 J=1,NDIM
      WRITE (2,111) ATOM2(J),ORB(J),(C(J,I),I=IST,MIN(IST+4,NVAL))
 120  CONTINUE
      IF (NVAL.LE.IST+4) GO TO 1000
      IST=IST+5
      GO TO 101
 110  FORMAT (/' EIGENVALUE',5(8X,F7.3,5X))
 111  FORMAT (3X,A2,4X,A2,5(3X,'(',F7.3,',',F7.3,')'))
C
 1000 RETURN
      END
```

Chapter 5

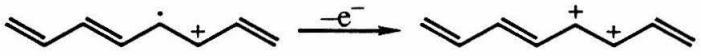
Conformational Studies of Cross-Conjugated Polymers: Polydimethylenecyclobutene and Polydiisopropylidenecyclobutene

A major part of the study of electrically conducting organic polymers is the elucidation of the mechanism of conduction in these systems. One proposed mechanism which currently enjoys popularity is one involving polarons, bipolarons, and solitons.[1] These are localized lattice distortions that are often associated with a positive or negative charge. As these distortions travel along the polymer chain, they carry along the associated charges, thereby producing electrical conduction.

A polaron is a radical cation (or anion) formed when an electron is removed (added) to the polymer backbone during a doping process.



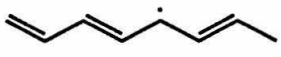
Since it has radical character, a polaron has a spin of 1/2 associated with it. Removal (or addition) of a second electron forms a bipolaron, which is doubly charged.



It has been shown that bipolaron formation is thermodynamically favored over the formation of two isolated polarons, in spite of the coulombic repulsion that accompanies the presence of two like charges in the same vicinity.[1] A bipolaron does not have radical character, so it is a spinless charge carrier.

Polarons and bipolarons can form in any conjugated polymer. In contrast, a soliton can be formed only when the polymer has a degenerate ground state, i.e., two geometric structures having the same total energy. An example is polyacetylene, in which the two structures differ by the exchange of single and double bonds.

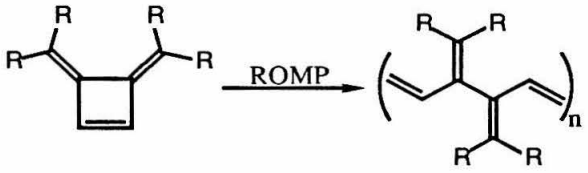
A soliton is a defect that marks the boundary between the two degenerate structures.



A neutral soliton (shown above) has radical character. Oxidative doping removes the unpaired electron and forms a positively-charged soliton, while reductive doping adds a second electron to pair with the existing one and forms a negatively-charged soliton.

Thus, a remarkable feature of solitons is that they can either have spin and no charge, or have charge but no spin. In this respect they are the exact opposite of polarons.

Conduction by polarons, bipolarons, or solitons is particularly appealing to organic chemists, since it can be represented by a simple "electron-pushing" formalism so widely used in discussing reaction mechanisms (Figure 1). This mechanism requires that the conducting polymer have a planar, conjugated backbone. This requirement is satisfied for most of the conducting polymers investigated to date. More recently, however, cross-conjugated polymer systems have been demonstrated to show substantial conductivities.[2–4] One example is polydiisopropylidenecyclobutene (**1**), formed by ring-opening metathesis polymerization (ROMP) of diisopropylidenecyclobutene.[3]



1 : R = CH_3
2 : R = H

The parent system, polydimethylenecyclobutene (**2**), is presumably also formed when dimethylenecyclobutene is ROMPed. However, **2** proved to be unstable to further processes such as crosslinking of the polymer chains.[3b]

A polaron- or bipolaron-mediated mechanism for conduction can still be envisoned for **1** (Figure 2), although this polymer has a cross-conjugated backbone. For this mechanism to work, however, it is still required that the polymer have a planar structure. In view of the steric interactions present in **1**, this appears to be unlikely. Yet, when doped with I_2 or AsF_5, the polymer shows substantial electrical conductivity.

The work described in this chapter was undertaken to investigate this apparent conflict. We have undertaken a theoretical study of the conformational preferences of **1** and **2** in both doped and undoped states. While the studies of **1** are more directly relevant to experiment, we have also studied **2** as the more fundamental parent system. We hope

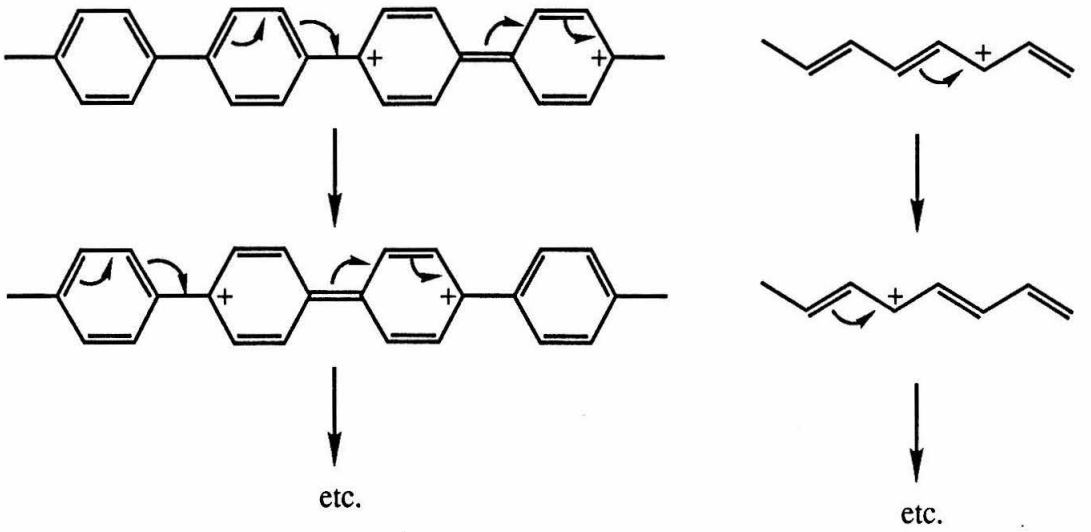


Figure 1. Conduction by bipolarons in polyphenylene (left) and by solitons in polyacetylene (right). Conduction by polarons is similar to bipolarons, except that one of the charged centers is replaced by a radical center.

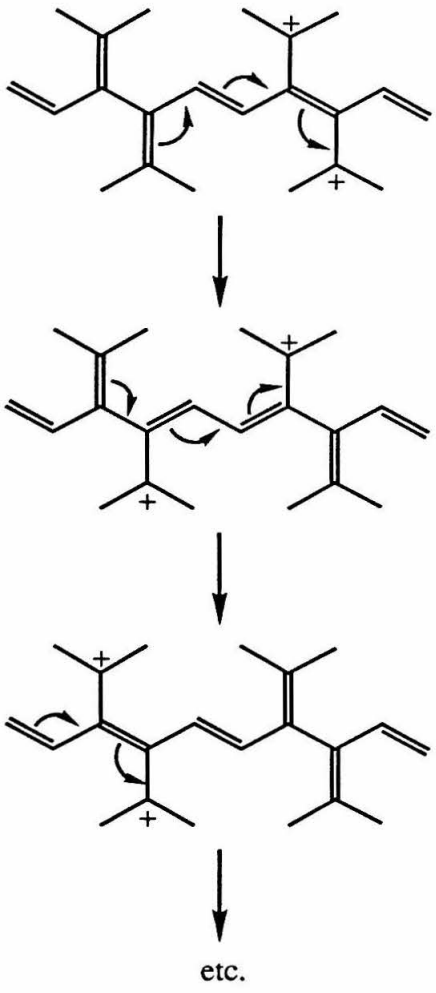


Figure 2. Conduction by bipolarons in **1**.

that the results, with rational modifications, can be applicable to other derivatives of this system.

Computational Methods

3,4-Diisopropylidene-1,5-hexadiene (**3**) and 3,4-dimethylene-1,5-hexadiene (**4**) were chosen as models for the unit cell of undoped **1** and **2**, respectively. For the doped polymers, the models chosen were 4,5-diisopropylidene-1,3,5,7-octatetraene dication (**5**) and 4,5-dimethylene-1,3,5,7-octatetraene dication (**6**).

MNDO[5] calculations were performed on **3**, **4**, **5**, and **6**. In these calculations, the geometries were partially optimized. All CC bond lengths, except those leading to the methyl groups in the models for **3** and **5**, were optimized. The CCC bond angles were also optimized in the models for **4** and **6**. Other parameters (CH bond lengths, bond angles, and torsion angles) were held constant. All the structures were constrained to have C_i symmetry.

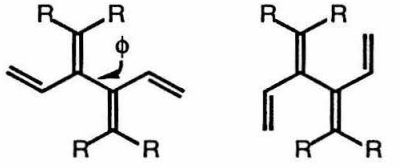
In addition to MNDO, calculations on **3**–**6** were also performed using extended Hückel (EH) theory.[6] The MNDO-optimized geometries were used for these calculations.

Calculations on the polymers themselves (**1** and **2**, as well as the doped systems $\mathbf{1}^{2+}$ and $\mathbf{2}^{2+}$) were performed using extended Hückel crystal orbital (EHCO) theory.[7] The geometries were based on the MNDO optimized geometries of **3**–**6**. In order to maintain translational symmetry, all the polymer calculations used a unit cell consisting of two six-carbon units for **2** and the corresponding ten-carbon units (including the methyl groups) for **1**; however, the energies shown below were calculated for a monomeric unit cell, i.e., one consisting of one such unit.

The MNDO calculations were performed using the AMPAC program;[8] the EH and EHCO calculations were performed using a program provided by Prof. Myung-Hwan Whangbo.

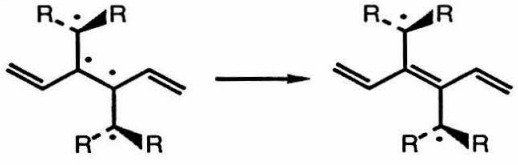
Results and Discussion

The choice of dimethylene- and diisopropylidenehexadienes (**4** and **3**) as models for the polymers **2** and **1** was obvious from consideration of the polymer's unit cell. Each molecule can be thought of as consisting of two butadiene units, connected by a single bond. Extensive preliminary calculations, as well as space-filling models, suggested that there is a substantial tendency of the torsion angle around this central bond (which we will designate as ϕ) to deviate from planarity. This tendency is comparatively small for the other torsion angles. Consequently, each half of the molecule (i.e., the butadiene units) were kept planar, while the energy of the molecule is calculated as a function of ϕ. Two possible conformations of the butadiene units, s-cis and s-trans, were considered, giving the conformers **A** and **B**, respectively.

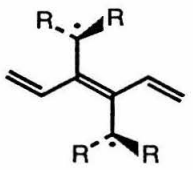


3A : R = CH_3 **3B** : R = CH_3
4A : R = H **4B** : R = H

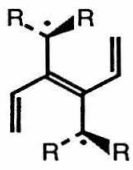
Two other conformations were considered. Substantial steric repulsions are present in these molecules, especially in **3** at the planar geometries (ϕ=0°). These repulsions may be reduced by deviation from planarity; however, they may also be reduced by twisting the methylene (in **4**) or the isopropylidene (in **3**) groups until they are perpendicular to the plane. This leads to the biradical structures dimethylene- and diisopropylidenehexatriene.



This alternative is also attractive since the polymeric analogue is simply a substituted polyacetylene, the best known conducting polymer. Once again, two conformations may be considered for each, giving the conformers **C** and **D**.

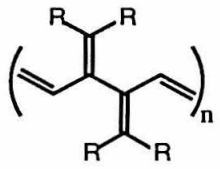


3C : R = CH_3
4C : R = H

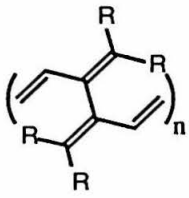


3D : R = CH_3
4D : R = H

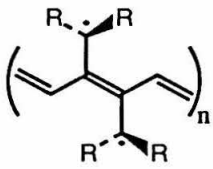
These four conformations serve as models for the four possible polymer conformations, also designated **A**–**D**.



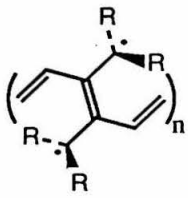
1A : R = CH_3
2A : R = H



1B : R = CH_3
2B : R = H



1C : R = CH_3
2C : R = H



1D : R = CH_3
2D : R = H

Results of the MNDO, EH (for **4** and **3**) and EHCO (for **2** and **1**) calculations are shown in Tables I and II and Figures 3 and 4. The results obtained from the three methods are generally in good agreement with each other, at least qualitatively. The only exceptions are the presence of a high barrier at ϕ=0° in the EHCO calculation for conformation **B** of the parent, which is absent in the MNDO and EH calculations (Figure 3), and the "reversed" shape of the EHCO curve for conformation **D**, also of the parent, compared to the MNDO and EH results (Figure 3).

In comparing the energies shown in Tables I and II and Figures 3 and 4, one must keep in mind that conformations **C** and **D** are open-shell structures (i.e, biradicals in the monomers, polyradicals in the polymers). Our calculations do not account for this; indeed, the extended Hückel method has no way of dealing with this problem. However, MNDO calculations on **3C** at the planar geometry, which included configuration

Table I. Relative energies of **4** (MNDO, EH) and relative energies per unit cell of **2** (EHCO) (eV).

	ϕ (degrees)	MNDO[a]	EH[b]	EHCO[c]
4A (2A)	0	0.5228	0.2706	0.3752
	20	0.4182	0.2113	0.2892
	40	0.2167	0.1290	0.1524
	60	0.0699	0.1194	0.2073
	80	0.0043	0.1319	0.2697
	100	0.0026	0.1238	0.2606
	120	0.0660	0.0957	0.1862
4B (2B)	0	1.2147	1.0320	3.6803
	20	0.9718	0.8071	2.2453
	40	0.4904	0.3622	0.6581
	60	0.1507	0.1036	0.1073
	80	0.0102	0.0364	0.0169
	100	0.0130	0.0295	0.0083
	120	0.1887	0.1439	0.1452
4C (2C)	0	4.3308	3.2264	3.1829
	30	4.3272	3.4446	3.2787
	60	4.5373	3.9587	3.4556
	90	4.7264	4.7639	3.4981
	120	4.7549	4.1456	3.5058
4D (2D)	0	4.6942	3.6990	4.3271
	30	4.7495	3.9445	4.0738
	60	4.8339	4.3594	3.6224
	90	4.9290	4.9615	3.4806
	120	5.0146	4.5402	3.6875

[a]The zero of energy corresponds to a heat of formation of 71.0 kcal/mol. [b]The zero of energy corresponds to a total energy of −748.4 eV. [c]The zero of energy corresponds to a total energy per unit cell of −534.0 eV.

Table II. Relative energies of **3** (MNDO, EH) and relative energies per unit cell of **1** (EHCO) (eV).

	ϕ (degrees)	MNDO[a]	EH[b]	EHCO[c]
3A (1A)	0	6.3497	4.8432	6.3697
	20	6.3401	4.4609	5.7438
	40	4.4538	3.5442	4.1145
	60	3.5652	2.9744	3.0188
	80	3.3439	2.9216	2.9392
	100	3.4513	2.9838	2.9958
	120	4.7557	3.8351	3.8156
3B (1B)	40	7.1312	3.0703	3.2314
	60	1.0722	0.8263	0.2776
	80	0.0047	0.0601	0.0312
	100	0.0557	0.0927	0.0675
	120	1.8601	1.4224	1.4126
3C (1C)	0	3.4532	2.7844	2.6934
	30	3.6270	3.0857	2.8946
	60	3.8490	3.6110	3.0642
	90	4.0292	4.1530	3.0811
	120	3.9731	3.6548	2.8765
3D (1D)	0	5.7790	4.4850	4.2842
	30	7.7942	5.3383	4.6369
	90	4.2927	4.1933	3.2011
	120	4.4790	4.1104	3.5109

[a]The zero of energy corresponds to a heat of formation of 64.0 kcal/mol. [b]The zero of energy corresponds to a total energy of −1175.1 eV. [c]The zero of energy corresponds to a total energy per unit cell of −960.8 eV.

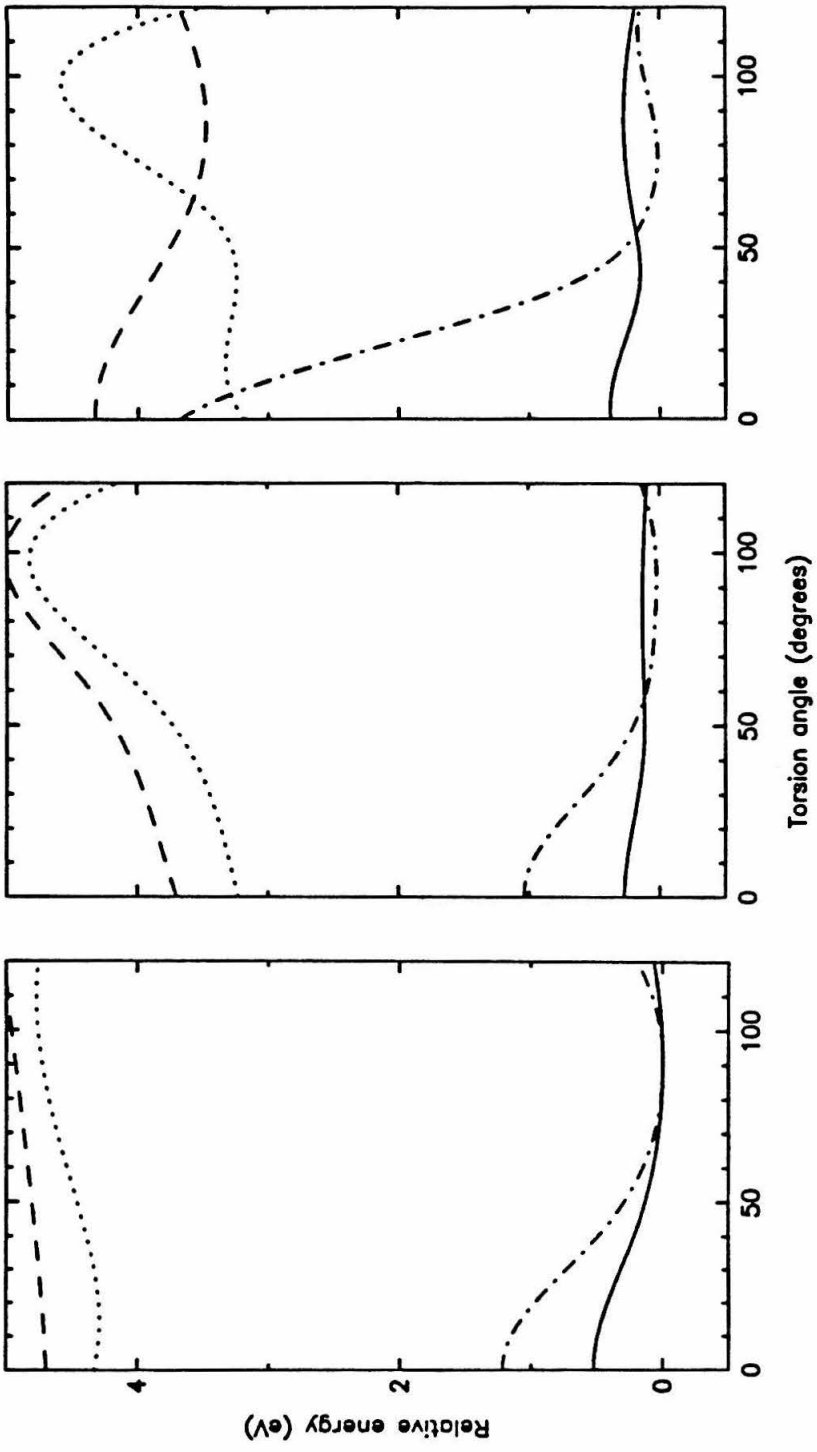


Figure 3. Relative MNDO (left) and EH (center) energies of **4** and relative EHCO energy per unit cell (right) of **2** as a function of ϕ. ———, conformation **A**; – · – · –, conformation **B**; · · · · · , conformation **C**; – – – –, conformation **D**.

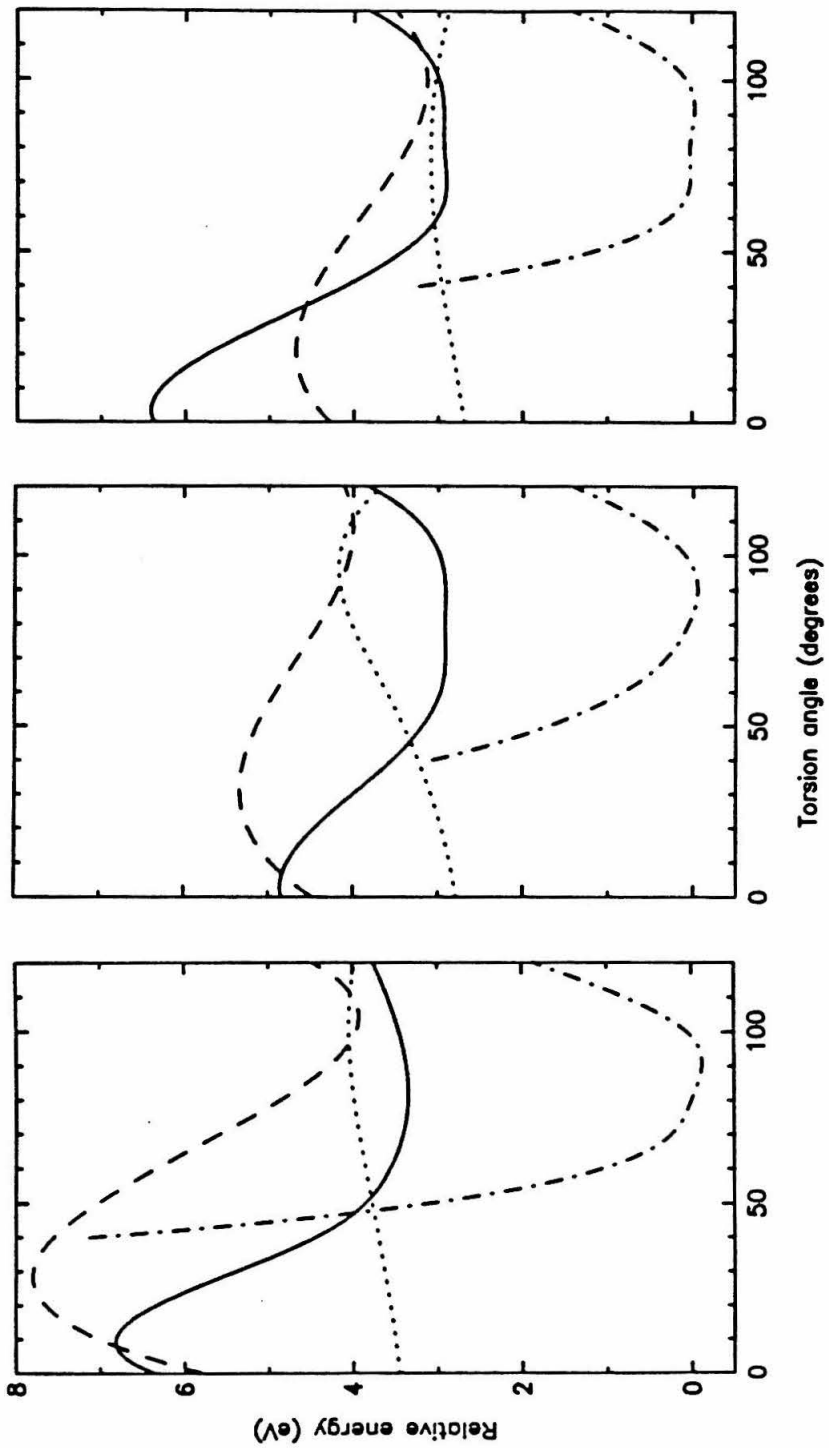


Figure 4. Relative MNDO (left) and EH (center) energies of **3** and relative EHCO energy per unit cell (right) of **1** as a function of ϕ. ———, conformation **A**; – · – · –, conformation **B**; · · · · · · , conformation **C**; – – – – –, conformation **D**.

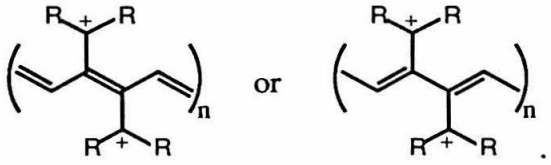
interaction (C.I.) to account for its biradical character, resulted in an energy about 2.5 eV lower than the energy shown in Table II. We can therefore shift the energy curves corresponding to conformations **C** and **D** in Figures 3 and 4 by this amount to obtain a more accurate representation of the relative energies (at least for the MNDO energy curves; there is no a priori reason to expect this correction to be applicable to the extended Hückel energies also).

For **1**, the lowest energy structure is quite obvious from Figure 4. It is **1B** with ϕ=90°, which corresponds to mutually perpendicular, all s-trans tetramethylhexatriene units. This result is not surprising when the steric interactions are considered. It is clear that the methyl groups experience severe steric repulsions with vinylic hydrogens in any planar conformation, forcing twisting around the single bonds. This result also agrees with the U.V. spectrum of **1**, which shows a single peak at 278 nm,[3] a wavelength consistent with a substituted hexatriene segment.[9]

For **2**, the steric repulsions are much less severe in the absence of the methyl groups, and the situation is not so clear-cut. As in **1**, the structure consisting of mutually perpendicular, all s-trans hexatriene units (**2B**, ϕ=90°) appears to be the best candidate for the ground state structure. However, **1A** is also a viable candidate, and the EH and EHCO calculations show little ϕ-dependence for this structure.

The structures discussed so far correspond to the polymers in their undoped state. Theoretical studies on polyparaphenylene[10] indicate a change from a nonplanar conformation in the undoped state (calculated to have a 37.8° torsion angle between rings; experimentally this torsion angle is found to be 23°[11]) to a nearly planar conformation (torsion angles 2.0°) upon reductive doping with lithium atoms. We therefore considered the possibility that polymers **1** and **2** adopt a different, perhaps more nearly planar, conformation upon oxidation.

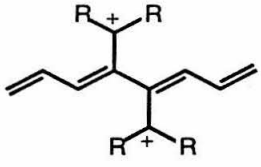
As mentioned above, we chose dimethylene- and diisopropylideneoctatetraene dications (**5** and **6**) as models for the doped polymers. We have chosen these rather than the dications of **3** and **4** for the following reason: The doped polymers correspond to substituted polyacetylenes, which can have one of two structures:



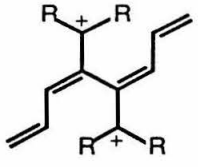
Of these two, we can expect the structure on the right to be preferred because of the availability of allyl resonance to delocalize the positive charge. In agreement with this expectation, MNDO calculations on the dications of **3** and **4**, which force a double bond between the substituted carbons, consistently resulted in a relatively long (ca. 1.5 Å) central bond, too long for a conjugated double bond. Thus, we feel that **5** and **6** would serve as better models for the doped polymers, which we designate $\mathbf{1}^{2+}$ and $\mathbf{2}^{2+}$.

The choice of **5** and **6** as models corresponds to the removal of two electrons per unit cell of the polymers. The actual doping levels necessary for conduction are *much* lower, but the models were chosen as extreme cases. In addition, the dications are even-electron, closed-shell species. Thus, the MNDO and extended Hückel calculations performed here should be meaningful.

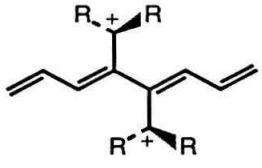
As in the undoped case, we have chosen four possible conformations of each "monomer",



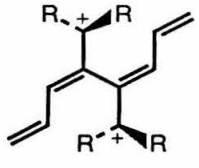
5A : R = CH_3
6A : R = H



5B : R = CH_3
6B : R = H

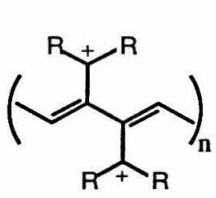


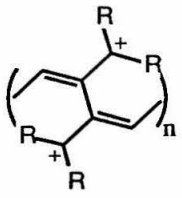
5C : R = CH_3
6C : R = H

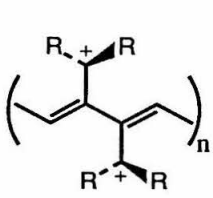


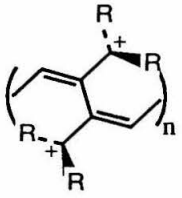
5D : R = CH_3
6D : R = H ,

corresponding to four possible conformation of each polymer,


$\mathbf{1A}^{2+}$: R = CH_3
$\mathbf{2A}^{2+}$: R = H


$\mathbf{1B}^{2+}$: R = CH_3
$\mathbf{2B}^{2+}$: R = H


$\mathbf{1C}^{2+}$: R = CH_3
$\mathbf{2C}^{2+}$: R = H


$\mathbf{1D}^{2+}$: R = CH_3
$\mathbf{2D}^{2+}$: R = H .

The results of these calculations are shown in Tables III and IV and Figures 5 and 6. Note that in this case there is no problem with biradical structures. All these structures, including conformations **C** and **D**, are closed-shell systems, and their energies can be directly compared to each other.

There is no appreciable change in the conformational preferences of **1** and **2** upon doping. For **1**, the global minimum unambiguously corresponds to a structure consisting of mutually perpendicular ten-carbon units (including the methyl groups), each having a fully extended, trans-like conformation. For **2**, the cis-like conformation is competitive in energy, and cannot be definitely ruled out as the ground state structure.

Another possibility for **1** emerges from the EH and EHCO energy profiles (Figure 6). There appears to be a secondary minimum, derived from conformation **C** at ϕ=0°, which is not too high in energy. This structure can be thought of as trans-polyacetylene substituted by orthogonal isopropyl cations. We considered the possibility that this is the conducting form of the polymer. However, the energies shown correspond to an unrealistically high doping level. With the much lower doping levels necessary for conduction, this structure would be expected to be substantially higher in energy.[12] Also, CP–MAS ^{13}C NMR spectra of doped **1** show no signals that would correspond to the essentially completely localized cationic carbons of $\mathbf{1}^{2+}\mathbf{C}$.[3] We thus consider it an unlikely candidate for the conducting form of **1**.

Given these results, we must conclude that the conduction mechanism in **1** cannot involve polarons and/or bipolarons. As discussed above, such a mechanism requires a planar structure, while we have demonstrated that **1** consists of essentially orthogonal

Table II. Relative energies of **6** (MNDO, EH) and relative energies per unit cell of 2^{2+} (EHCO) (eV).

	ϕ (degrees)	MNDO[a]	EH[b]	EHCO[c]
6A ($2A^{2+}$)	0	0.5851	0.3179	0.3454
	20	0.4779	0.2545	0.1963
	40	0.2570	0.1586	0.0967
	60	0.0845	0.1461	0.1344
	80	0.0044	0.1798	0.2071
	100	0.0156	0.1779	0.2074
	120	0.1169	0.1558	0.1756
6B ($2B^{2+}$)	0	1.2588	1.0155	3.4487
	20	1.0190	0.8046	2.2939
	40	0.5405	0.4349	0.5294
	60	0.1944	0.1487	0.0766
	80	0.0542	0.1008	0.0215
	100	0.0827	0.0975	0.0236
	120	0.2962	0.1681	0.1036
6C ($2C^{2+}$)	0	3.0553	1.5336	0.9843
	20	2.9881	1.5680	1.0464
	40	2.8667	1.5414	1.1616
	60	2.7307	1.4969	1.3412
	80	2.6709	1.5188	1.3802
	100	2.7431	1.5596	1.3020
	120	2.9187	1.5626	1.1637
6D ($2D^{2+}$)	0	3.3457	1.6395	1.1014
	20	3.3327	1.7545	1.2528
	40	3.1947	1.8011	1.2885
	60	2.9295	1.6625	1.3199
	80	2.8104	1.5660	1.3588
	100	2.8913	1.6242	1.2566
	120	3.1748	1.7019	1.2404

[a]The zero of energy corresponds to a heat of formation of 517.0 kcal/mol. [b]The zero of energy corresponds to a total energy of –903.0 eV. [c]The zero of energy corresponds to a total energy per unit cell of –510.0 eV.

Table II. Relative energies of **5** (MNDO, EH) and relative energies per unit cell of $\mathbf{1}^{2+}$ (EHCO) (eV).

	ϕ (degrees)	MNDO[a]	EH[b]	EHCO[c]
5A ($\mathbf{1A}^{2+}$)	0	6.2912	5.0820	6.8506
	20	5.8359	4.6970	6.1360
	40	4.4715	3.9179	4.3648
	60	3.6023	3.4659	3.4907
	80	3.3529	3.4185	3.3200
	100	3.4389	3.4446	3.3331
	120	4.6004	4.0174	3.8464
5B ($\mathbf{1B}^{2+}$)	40	7.1642	2.8578	3.1077
	60	1.1433	0.7435	0.6490
	80	0.0403	0.0601	0.0286
	100	0.0927	0.0881	0.0651
	120	1.7887	1.1668	1.2017
5C ($\mathbf{1C}^{2+}$)	0	1.6640	0.2633	0.1789
	20	1.6797	0.3122	0.1958
	40	1.6516	0.3750	0.2863
	60	1.5181	0.3833	0.3299
	80	1.4492	0.3963	0.3643
	100	1.5053	0.4118	0.3769
	120	1.5836	0.3605	0.2788
5D ($\mathbf{1D}^{2+}$)	0	3.9070	1.5616	1.4348
	20	5.2837	2.7124	2.4761
	40	6.3663	2.7357	2.4619
	60	4.2521	2.3850	2.2326
	80	2.0545	0.7590	0.7158
	100	1.7040	0.4834	0.4499
	120	2.0660	0.7038	0.9226

[a]The zero of energy corresponds to a heat of formation of 501.0 kcal/mol. [b]The zero of energy corresponds to a total energy of −1330.2 eV. [c]The zero of energy corresponds to a total energy per unit cell of −937.7 eV.

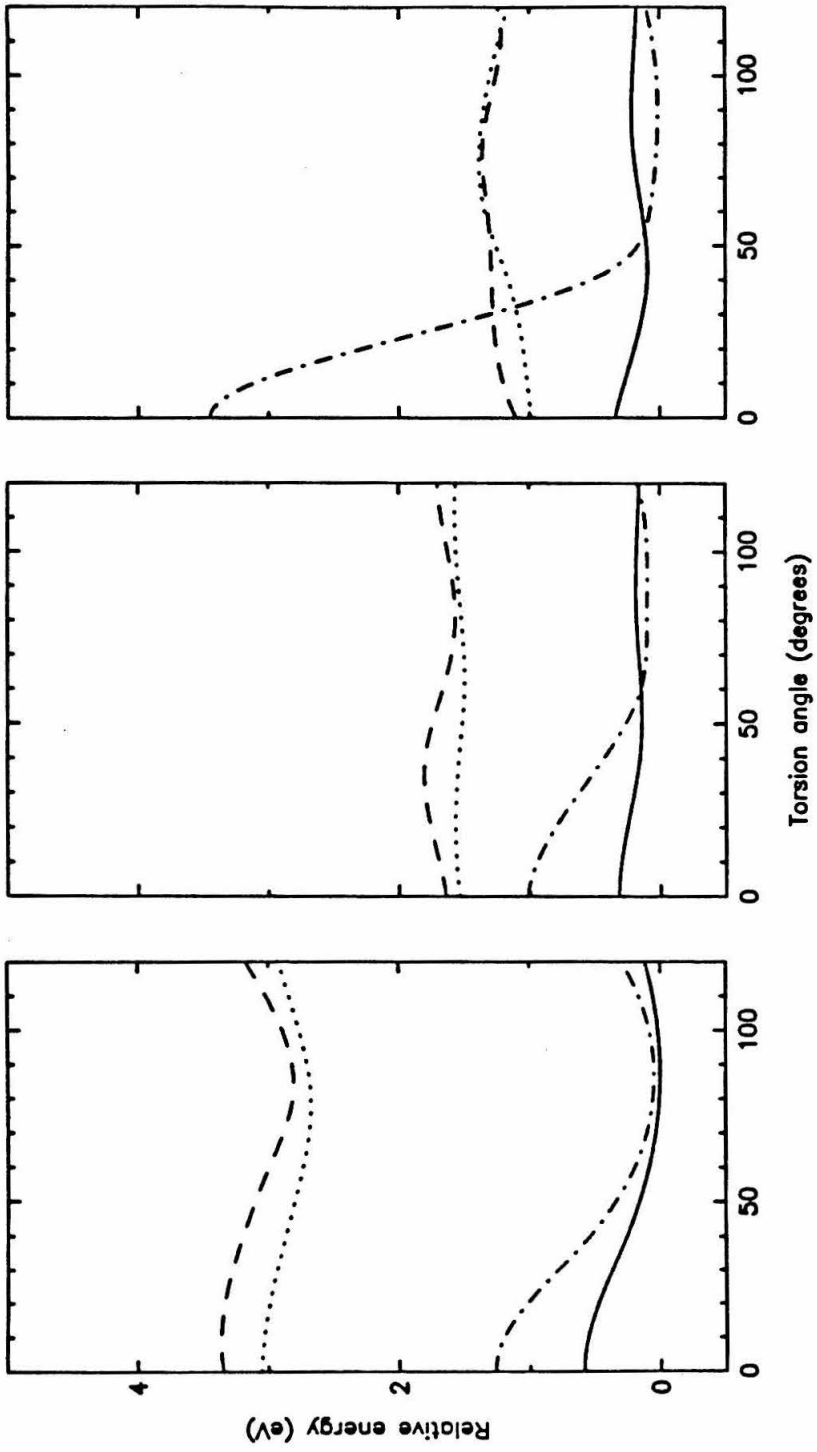


Figure 5. Relative MNDO (left) and EH (center) energies of **6** and relative EHCO energy per unit cell (right) of 2^{2+} as a function of ϕ. ———— , conformation **A**; – · – · – , conformation **B**; · · · · · , conformation **C**; – – – – , conformation **D**.

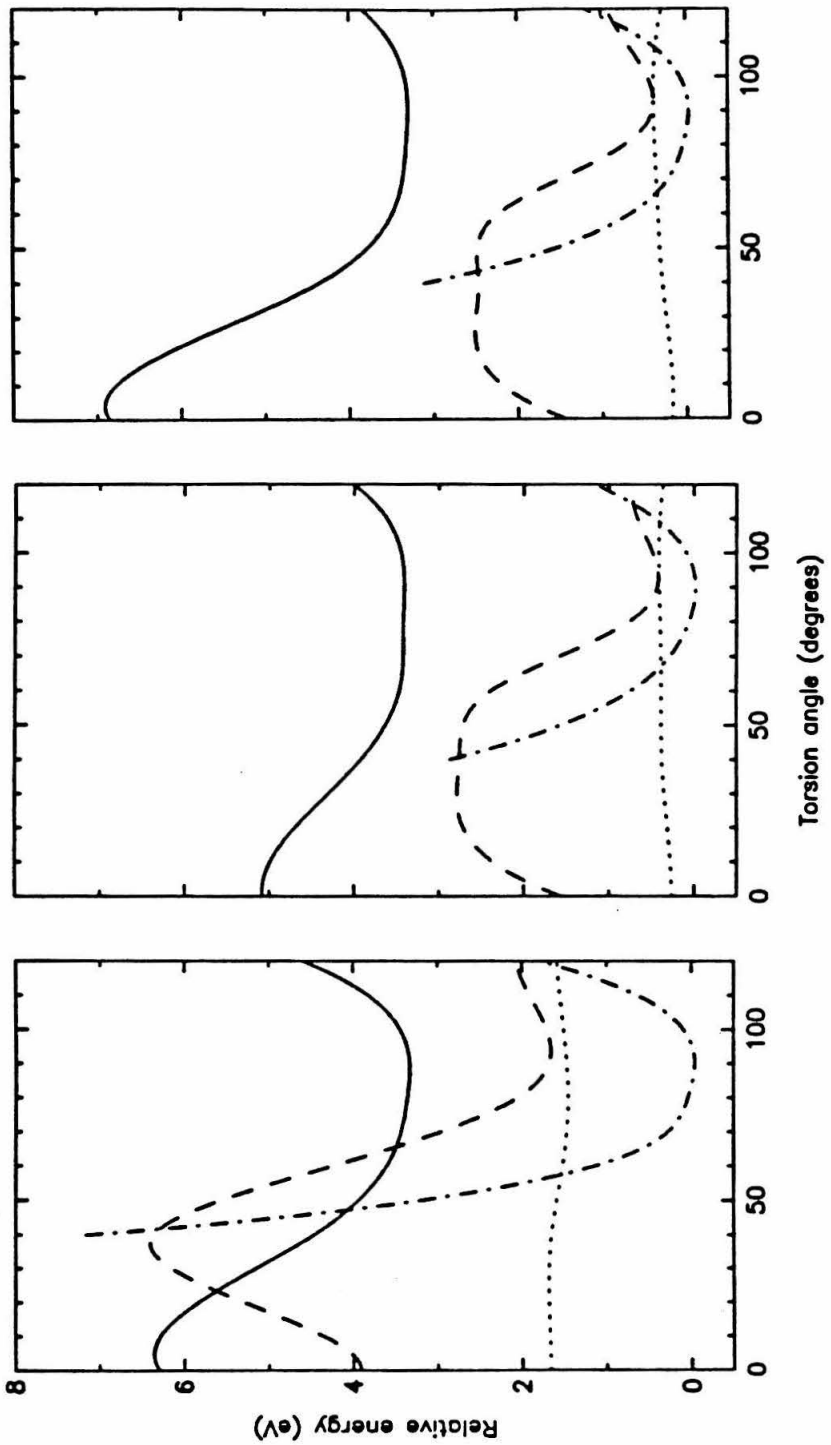


Figure 6. Relative MNDO (left) and EH (center) energies of **5** and relative EHCO energy per unit cell (right) of $\mathbf{1}^{2+}$ as a function of ϕ. ———— , conformation **A**; – · – · – , conformation **B**; · · · · · , conformation **C**; – – – – , conformation **D**.

hexatriene units. Several alternative conduction mechanisms have been proposed for conducting polymers.[13,14] Most of these involve intra- and interchain charge transfer, with the current being carried by electrons or "holes", as in conventional inorganic conductors and semiconductors. Whether this is the conduction mechanism in polymers like **1** remains to be seen.

Conclusions

We have determined the structure of **1** to consist of mutually perpendicular hexatriene units. The same structure may be expected for **2**, although the evidence here is not as compelling. No conformational change is expected upon doping. Such a structure is incompatible with conventional conduction mechanisms involving polarons or bipolarons. Thus, **1** must conduct by a different mechanism, possibly involving charge transfer within and among polymer chains.

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(12) It might be argued that the negatively charged counterions would stabilize the localized cations in $\mathbf{1}^{2+}\mathbf{C}$ more than the delocalized ones in $\mathbf{1}^{2+}\mathbf{B}$. We have also considered this possibility by performing MNDO calculations with the inclusion of negative "sparkles" (which are localized spherical charges) to represent the counterions. Although **5C** was indeed stabilized more than **5B**, the preferential stabilization was not sufficient to compensate for the original energy difference.

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Appendix: Z-matrices

Complete geometry specifications of the structures described in this chapter are given on the following pages in the form of Z-matrices. Only the geometries used for MNDO and EH calculations are given; geometries for the EHCO calculations can be derived easily from these. Angles are rounded off to the nearest degree.

4A, ϕ = 0°:

1	C						
2	C	1	1.3558				
3	C	2	1.4831	1	128.0		
4	C	3	1.5078	2	118.0	1	180.0
5	C	4	1.4831	3	118.0	2	180.0
6	C	5	1.3558	4	128.0	3	180.0
7	C	3	1.3660	2	119.0	1	0.0
8	C	4	1.3660	5	119.0	6	0.0
9	H	1	1.0800	2	120.0	3	180.0
10	H	1	1.0800	2	120.0	3	0.0
11	H	2	1.0800	3	120.0	1	180.0
12	H	7	1.0800	3	120.0	2	0.0
13	H	7	1.0800	3	120.0	2	180.0
14	H	8	1.0800	4	120.0	5	0.0
15	H	8	1.0800	4	120.0	5	180.0
16	H	5	1.0800	4	120.0	6	180.0
17	H	6	1.0800	5	120.0	4	180.0
18	H	6	1.0800	5	120.0	4	0.0

4A, ϕ = 20°:

1	C						
2	C	1	1.3557				
3	C	2	1.4811	1	128.0		
4	C	3	1.5070	2	118.0	1	180.0
5	C	4	1.4811	3	118.0	2	160.0
6	C	5	1.3557	4	128.0	3	180.0
7	C	3	1.3649	2	120.0	1	0.0
8	C	4	1.3649	5	120.0	6	0.0
9	H	1	1.0800	2	120.0	3	180.0
10	H	1	1.0800	2	120.0	3	0.0
11	H	2	1.0800	3	120.0	1	180.0
12	H	7	1.0800	3	120.0	2	0.0
13	H	7	1.0800	3	120.0	2	180.0
14	H	8	1.0800	4	120.0	5	0.0
15	H	8	1.0800	4	120.0	5	180.0
16	H	5	1.0800	4	120.0	6	180.0
17	H	6	1.0800	5	120.0	4	180.0
18	H	6	1.0800	5	120.0	4	0.0

4A, ϕ = 40°:

1	C						
2	C	1	1.3555				
3	C	2	1.4773	1	127.0		
4	C	3	1.5056	2	116.0	1	180.0
5	C	4	1.4773	3	116.0	2	140.0
6	C	5	1.3555	4	127.0	3	180.0
7	C	3	1.3623	2	123.0	1	0.0
8	C	4	1.3623	5	123.0	6	0.0
9	H	1	1.0800	2	120.0	3	180.0
10	H	1	1.0800	2	120.0	3	0.0
11	H	2	1.0800	3	120.0	1	180.0
12	H	7	1.0800	3	120.0	2	0.0
13	H	7	1.0800	3	120.0	2	180.0
14	H	8	1.0800	4	120.0	5	0.0
15	H	8	1.0800	4	120.0	5	180.0
16	H	5	1.0800	4	120.0	6	180.0
17	H	6	1.0800	5	120.0	4	180.0
18	H	6	1.0800	5	120.0	4	0.0

4A, ϕ = 60°:

1	C						
2	C	1	1.3554				
3	C	2	1.4743	1	127.0		
4	C	3	1.5055	2	115.0	1	180.0
5	C	4	1.4743	3	115.0	2	120.0
6	C	5	1.3554	4	127.0	3	180.0
7	C	3	1.3596	2	125.0	1	0.0
8	C	4	1.3596	5	125.0	6	0.0
9	H	1	1.0800	2	120.0	3	180.0
10	H	1	1.0800	2	120.0	3	0.0
11	H	2	1.0800	3	120.0	1	180.0
12	H	7	1.0800	3	120.0	2	0.0
13	H	7	1.0800	3	120.0	2	180.0
14	H	8	1.0800	4	120.0	5	0.0
15	H	8	1.0800	4	120.0	5	180.0
16	H	5	1.0800	4	120.0	6	180.0
17	H	6	1.0800	5	120.0	4	180.0
18	H	6	1.0800	5	120.0	4	0.0

4A, ϕ = 80°:

1	C						
2	C	1	1.3554				
3	C	2	1.4730	1	127.0		
4	C	3	1.5056	2	115.0	1	180.0
5	C	4	1.4730	3	115.0	2	100.0
6	C	5	1.3554	4	127.0	3	180.0
7	C	3	1.3580	2	126.0	1	0.0
8	C	4	1.3580	5	126.0	6	0.0
9	H	1	1.0800	2	120.0	3	180.0
10	H	1	1.0800	2	120.0	3	0.0
11	H	2	1.0800	3	120.0	1	180.0
12	H	7	1.0800	3	120.0	2	0.0
13	H	7	1.0800	3	120.0	2	180.0
14	H	8	1.0800	4	120.0	5	0.0
15	H	8	1.0800	4	120.0	5	180.0
16	H	5	1.0800	4	120.0	6	180.0
17	H	6	1.0800	5	120.0	4	180.0
18	H	6	1.0800	5	120.0	4	0.0

4A, ϕ = 100°:

1	C						
2	C	1	1.3555				
3	C	2	1.4729	1	127.0		
4	C	3	1.5044	2	115.0	1	180.0
5	C	4	1.4729	3	115.0	2	80.0
6	C	5	1.3555	4	127.0	3	180.0
7	C	3	1.3582	2	126.0	1	0.0
8	C	4	1.3582	5	126.0	6	0.0
9	H	1	1.0800	2	120.0	3	180.0
10	H	1	1.0800	2	120.0	3	0.0
11	H	2	1.0800	3	120.0	1	180.0
12	H	7	1.0800	3	120.0	2	0.0
13	H	7	1.0800	3	120.0	2	180.0
14	H	8	1.0800	4	120.0	5	0.0
15	H	8	1.0800	4	120.0	5	180.0
16	H	5	1.0800	4	120.0	6	180.0
17	H	6	1.0800	5	120.0	4	180.0
18	H	6	1.0800	5	120.0	4	0.0

4A, $\phi = 120°$:

1	C						
2	C	1	1.3554				
3	C	2	1.4744	1	127.0		
4	C	3	1.5046	2	115.0	1	180.0
5	C	4	1.4744	3	115.0	2	60.0
6	C	5	1.3554	4	127.0	3	180.0
7	C	3	1.3596	2	125.0	1	0.0
8	C	4	1.3596	5	125.0	6	0.0
9	H	1	1.0800	2	120.0	3	180.0
10	H	1	1.0800	2	120.0	3	0.0
11	H	2	1.0800	3	120.0	1	180.0
12	H	7	1.0800	3	120.0	2	0.0
13	H	7	1.0800	3	120.0	2	180.0
14	H	8	1.0800	4	120.0	5	0.0
15	H	8	1.0800	4	120.0	5	180.0
16	H	5	1.0800	4	120.0	6	180.0
17	H	6	1.0800	5	120.0	4	180.0
18	H	6	1.0800	5	120.0	4	0.0

4B, ϕ = 0°:

1	C						
2	C	1	1.3567				
3	C	2	1.4893	1	134.0		
4	C	3	1.4944	2	127.0	1	0.0
5	C	4	1.4893	3	127.0	2	180.0
6	C	5	1.3567	4	134.0	3	0.0
7	C	3	1.3710	2	109.0	1	180.0
8	C	4	1.3710	5	109.0	6	180.0
9	H	1	1.0800	2	120.0	3	180.0
10	H	1	1.0800	2	120.0	3	0.0
11	H	2	1.0800	3	120.0	1	180.0
12	H	7	1.0800	3	120.0	2	0.0
13	H	7	1.0800	3	120.0	2	180.0
14	H	8	1.0800	4	120.0	5	0.0
15	H	8	1.0800	4	120.0	5	180.0
16	H	5	1.0800	4	120.0	6	180.0
17	H	6	1.0800	5	120.0	4	180.0
18	H	6	1.0800	5	120.0	4	0.0

4B, ϕ = 20°:

1	C						
2	C	1	1.3562				
3	C	2	1.4865	1	133.0		
4	C	3	1.4938	2	126.0	1	0.0
5	C	4	1.4865	3	126.0	2	160.0
6	C	5	1.3562	4	133.0	3	0.0
7	C	3	1.3695	2	111.0	1	180.0
8	C	4	1.3695	5	111.0	6	180.0
9	H	1	1.0800	2	120.0	3	180.0
10	H	1	1.0800	2	120.0	3	0.0
11	H	2	1.0800	3	120.0	1	180.0
12	H	7	1.0800	3	120.0	2	0.0
13	H	7	1.0800	3	120.0	2	180.0
14	H	8	1.0800	4	120.0	5	0.0
15	H	8	1.0800	4	120.0	5	180.0
16	H	5	1.0800	4	120.0	6	180.0
17	H	6	1.0800	5	120.0	4	180.0
18	H	6	1.0800	5	120.0	4	0.0

4B, ϕ = 40°:

1	C						
2	C	1	1.3554				
3	C	2	1.4812	1	130.0		
4	C	3	1.4940	2	123.0	1	0.0
5	C	4	1.4812	3	123.0	2	140.0
6	C	5	1.3554	4	130.0	3	0.0
7	C	3	1.3660	2	115.0	1	180.0
8	C	4	1.3660	5	115.0	6	180.0
9	H	1	1.0800	2	120.0	3	180.0
10	H	1	1.0800	2	120.0	3	0.0
11	H	2	1.0800	3	120.0	1	180.0
12	H	7	1.0800	3	120.0	2	0.0
13	H	7	1.0800	3	120.0	2	180.0
14	H	8	1.0800	4	120.0	5	0.0
15	H	8	1.0800	4	120.0	5	180.0
16	H	5	1.0800	4	120.0	6	180.0
17	H	6	1.0800	5	120.0	4	180.0
18	H	6	1.0800	5	120.0	4	0.0

4B, ϕ = 60°:

1	C						
2	C	1	1.3547				
3	C	2	1.4775	1	127.0		
4	C	3	1.4955	2	121.0	1	0.0
5	C	4	1.4775	3	121.0	2	120.0
6	C	5	1.3547	4	127.0	3	0.0
7	C	3	1.3622	2	119.0	1	180.0
8	C	4	1.3622	5	119.0	6	180.0
9	H	1	1.0800	2	120.0	3	180.0
10	H	1	1.0800	2	120.0	3	0.0
11	H	2	1.0800	3	120.0	1	180.0
12	H	7	1.0800	3	120.0	2	0.0
13	H	7	1.0800	3	120.0	2	180.0
14	H	8	1.0800	4	120.0	5	0.0
15	H	8	1.0800	4	120.0	5	180.0
16	H	5	1.0800	4	120.0	6	180.0
17	H	6	1.0800	5	120.0	4	180.0
18	H	6	1.0800	5	120.0	4	0.0

4B, ϕ = 80°:

1	C						
2	C	1	1.3544				
3	C	2	1.4755	1	126.0		
4	C	3	1.4969	2	120.0	1	0.0
5	C	4	1.4755	3	120.0	2	100.0
6	C	5	1.3544	4	126.0	3	0.0
7	C	3	1.3599	2	120.0	1	180.0
8	C	4	1.3599	5	120.0	6	180.0
9	H	1	1.0800	2	120.0	3	180.0
10	H	1	1.0800	2	120.0	3	0.0
11	H	2	1.0800	3	120.0	1	180.0
12	H	7	1.0800	3	120.0	2	0.0
13	H	7	1.0800	3	120.0	2	180.0
14	H	8	1.0800	4	120.0	5	0.0
15	H	8	1.0800	4	120.0	5	180.0
16	H	5	1.0800	4	120.0	6	180.0
17	H	6	1.0800	5	120.0	4	180.0
18	H	6	1.0800	5	120.0	4	0.0

4B, ϕ = 100°:

1	C						
2	C	1	1.3543				
3	C	2	1.4750	1	126.0		
4	C	3	1.4965	2	120.0	1	0.0
5	C	4	1.4750	3	120.0	2	80.0
6	C	5	1.3543	4	126.0	3	0.0
7	C	3	1.3600	2	120.0	1	180.0
8	C	4	1.3600	5	120.0	6	180.0
9	H	1	1.0800	2	120.0	3	180.0
10	H	1	1.0800	2	120.0	3	0.0
11	H	2	1.0800	3	120.0	1	180.0
12	H	7	1.0800	3	120.0	2	0.0
13	H	7	1.0800	3	120.0	2	180.0
14	H	8	1.0800	4	120.0	5	0.0
15	H	8	1.0800	4	120.0	5	180.0
16	H	5	1.0800	4	120.0	6	180.0
17	H	6	1.0800	5	120.0	4	180.0
18	H	6	1.0800	5	120.0	4	0.0

4B, $\phi = 120°$:

1	C						
2	C	1	1.3550				
3	C	2	1.4762	1	128.0		
4	C	3	1.4958	2	122.0	1	0.0
5	C	4	1.4762	3	122.0	2	60.0
6	C	5	1.3550	4	128.0	3	0.0
7	C	3	1.3634	2	118.0	1	180.0
8	C	4	1.3634	5	118.0	6	180.0
9	H	1	1.0800	2	120.0	3	180.0
10	H	1	1.0800	2	120.0	3	0.0
11	H	2	1.0800	3	120.0	1	180.0
12	H	7	1.0800	3	120.0	2	0.0
13	H	7	1.0800	3	120.0	2	180.0
14	H	8	1.0800	4	120.0	5	0.0
15	H	8	1.0800	4	120.0	5	180.0
16	H	5	1.0800	4	120.0	6	180.0
17	H	6	1.0800	5	120.0	4	180.0
18	H	6	1.0800	5	120.0	4	0.0

4C, $\phi = 0°$:

1	C						
2	C	1	1.3551				
3	C	2	1.4763	1	126.0		
4	C	3	1.4014	2	120.0	1	180.0
5	C	4	1.4763	3	120.0	2	180.0
6	C	5	1.3551	4	126.0	3	180.0
7	C	3	1.4316	2	119.0	1	0.0
8	C	4	1.4316	5	119.0	6	0.0
9	H	1	1.0800	2	120.0	3	180.0
10	H	1	1.0800	2	120.0	3	0.0
11	H	2	1.0800	3	120.0	1	180.0
12	H	7	1.0800	3	120.0	2	90.0
13	H	7	1.0800	3	120.0	2	-90.0
14	H	8	1.0800	4	120.0	5	90.0
15	H	8	1.0800	4	120.0	5	-90.0
16	H	5	1.0800	4	120.0	6	180.0
17	H	6	1.0800	5	120.0	4	180.0
18	H	6	1.0800	5	120.0	4	0.0

4C, $\phi = 30°$:

1	C						
2	C	1	1.3590				
3	C	2	1.4623	1	125.0		
4	C	3	1.4459	2	119.0	1	180.0
5	C	4	1.4623	3	119.0	2	150.0
6	C	5	1.3590	4	125.0	3	180.0
7	C	3	1.4205	2	121.0	1	0.0
8	C	4	1.4205	5	121.0	6	0.0
9	H	1	1.0800	2	120.0	3	180.0
10	H	1	1.0800	2	120.0	3	0.0
11	H	2	1.0800	3	120.0	1	180.0
12	H	7	1.0800	3	120.0	2	90.0
13	H	7	1.0800	3	120.0	2	-90.0
14	H	8	1.0800	4	120.0	5	90.0
15	H	8	1.0800	4	120.0	5	-90.0
16	H	5	1.0800	4	120.0	6	180.0
17	H	6	1.0800	5	120.0	4	180.0
18	H	6	1.0800	5	120.0	4	0.0

4C, $\phi = 60°$:

1	C						
2	C	1	1.3609				
3	C	2	1.4536	1	125.0		
4	C	3	1.4754	2	117.0	1	180.0
5	C	4	1.4536	3	117.0	2	120.0
6	C	5	1.3609	4	125.0	3	180.0
7	C	3	1.4142	2	123.0	1	0.0
8	C	4	1.4142	5	123.0	6	0.0
9	H	1	1.0800	2	120.0	3	180.0
10	H	1	1.0800	2	120.0	3	0.0
11	H	2	1.0800	3	120.0	1	180.0
12	H	7	1.0800	3	120.0	2	90.0
13	H	7	1.0800	3	120.0	2	-90.0
14	H	8	1.0800	4	120.0	5	90.0
15	H	8	1.0800	4	120.0	5	-90.0
16	H	5	1.0800	4	120.0	6	180.0
17	H	6	1.0800	5	120.0	4	180.0
18	H	6	1.0800	5	120.0	4	0.0

4C, ϕ = 90°:

1	C						
2	C	1	1.3624				
3	C	2	1.4487	1	125.0		
4	C	3	1.4908	2	116.0	1	180.0
5	C	4	1.4487	3	116.0	2	90.0
6	C	5	1.3624	4	125.0	3	180.0
7	C	3	1.4132	2	124.0	1	0.0
8	C	4	1.4132	5	124.0	6	0.0
9	H	1	1.0800	2	120.0	3	180.0
10	H	1	1.0800	2	120.0	3	0.0
11	H	2	1.0800	3	120.0	1	180.0
12	H	7	1.0800	3	120.0	2	90.0
13	H	7	1.0800	3	120.0	2	-90.0
14	H	8	1.0800	4	120.0	5	90.0
15	H	8	1.0800	4	120.0	5	-90.0
16	H	5	1.0800	4	120.0	6	180.0
17	H	6	1.0800	5	120.0	4	180.0
18	H	6	1.0800	5	120.0	4	0.0

4C, ϕ = 120°:

1	C						
2	C	1	1.3623				
3	C	2	1.4501	1	125.0		
4	C	3	1.4669	2	119.0	1	180.0
5	C	4	1.4501	3	119.0	2	60.0
6	C	5	1.3623	4	125.0	3	180.0
7	C	3	1.4267	2	122.0	1	0.0
8	C	4	1.4267	5	122.0	6	0.0
9	H	1	1.0800	2	120.0	3	180.0
10	H	1	1.0800	2	120.0	3	0.0
11	H	2	1.0800	3	120.0	1	180.0
12	H	7	1.0800	3	120.0	2	90.0
13	H	7	1.0800	3	120.0	2	-90.0
14	H	8	1.0800	4	120.0	5	90.0
15	H	8	1.0800	4	120.0	5	-90.0
16	H	5	1.0800	4	120.0	6	180.0
17	H	6	1.0800	5	120.0	4	180.0
18	H	6	1.0800	5	120.0	4	0.0

4D, ϕ = 0°:

1	C						
2	C	1	1.3559				
3	C	2	1.4784	1	129.0		
4	C	3	1.3919	2	127.0	1	0.0
5	C	4	1.4784	3	127.0	2	180.0
6	C	5	1.3559	4	129.0	3	0.0
7	C	3	1.4382	2	111.0	1	180.0
8	C	4	1.4382	5	111.0	6	180.0
9	H	1	1.0800	2	120.0	3	180.0
10	H	1	1.0800	2	120.0	3	0.0
11	H	2	1.0800	3	120.0	1	180.0
12	H	7	1.0800	3	120.0	2	90.0
13	H	7	1.0800	3	120.0	2	-90.0
14	H	8	1.0800	4	120.0	5	90.0
15	H	8	1.0800	4	120.0	5	-90.0
16	H	5	1.0800	4	120.0	6	180.0
17	H	6	1.0800	5	120.0	4	180.0
18	H	6	1.0800	5	120.0	4	0.0

4D, ϕ = 30°:

1	C						
2	C	1	1.3577				
3	C	2	1.4684	1	129.0		
4	C	3	1.4298	2	126.0	1	0.0
5	C	4	1.4694	3	126.0	2	150.0
6	C	5	1.3577	4	129.0	3	0.0
7	C	3	1.4280	2	113.0	1	180.0
8	C	4	1.4280	5	113.0	6	180.0
9	H	1	1.0800	2	120.0	3	180.0
10	H	1	1.0800	2	120.0	3	0.0
11	H	2	1.0800	3	120.0	1	180.0
12	H	7	1.0800	3	120.0	2	90.0
13	H	7	1.0800	3	120.0	2	-90.0
14	H	8	1.0800	4	120.0	5	90.0
15	H	8	1.0800	4	120.0	5	-90.0
16	H	5	1.0800	4	120.0	6	180.0
17	H	6	1.0800	5	120.0	4	180.0
18	H	6	1.0800	5	120.0	4	0.0

4D, ϕ = 60°:

1	C						
2	C	1	1.3594				
3	C	2	1.4578	1	128.0		
4	C	3	1.4649	2	123.0	1	0.0
5	C	4	1.4578	3	123.0	2	120.0
6	C	5	1.3594	4	128.0	3	0.0
7	C	3	1.4120	2	117.0	1	180.0
8	C	4	1.4120	5	117.0	6	180.0
9	H	1	1.0800	2	120.0	3	180.0
10	H	1	1.0800	2	120.0	3	0.0
11	H	2	1.0800	3	120.0	1	180.0
12	H	7	1.0800	3	120.0	2	90.0
13	H	7	1.0800	3	120.0	2	-90.0
14	H	8	1.0800	4	120.0	5	90.0
15	H	8	1.0800	4	120.0	5	-90.0
16	H	5	1.0800	4	120.0	6	180.0
17	H	6	1.0800	5	120.0	4	180.0
18	H	6	1.0800	5	120.0	4	0.0

4D, ϕ = 90°:

```
 1     C
 2     C      1     1.3605
 3     C      2     1.4532     1     127.0
 4     C      3     1.4843     2     120.0      1       0.0
 5     C      4     1.4532     3     120.0      2      90.0
 6     C      5     1.3605     4     127.0      3       0.0
 7     C      3     1.4163     2     119.0      1     180.0
 8     C      4     1.4163     5     119.0      6     180.0
 9     H      1     1.0800     2     120.0      3     180.0
10     H      1     1.0800     2     120.0      3       0.0
11     H      2     1.0800     3     120.0      1     180.0
12     H      7     1.0800     3     120.0      2      90.0
13     H      7     1.0800     3     120.0      2     -90.0
14     H      8     1.0800     4     120.0      5      90.0
15     H      8     1.0800     4     120.0      5     -90.0
16     H      5     1.0800     4     120.0      6     180.0
17     H      6     1.0800     5     120.0      4     180.0
18     H      6     1.0800     5     120.0      4       0.0
```

4D, ϕ = 120°:

```
 1     C
 2     C      1     1.3600
 3     C      2     1.4553     1     127.0
 4     C      3     1.4517     2     126.0      1       0.0
 5     C      4     1.4553     3     126.0      2      60.0
 6     C      5     1.3600     4     127.0      3       0.0
 7     C      3     1.4344     2     117.0      1     180.0
 8     C      4     1.4344     5     117.0      6     180.0
 9     H      1     1.0800     2     120.0      3     180.0
10     H      1     1.0800     2     120.0      3       0.0
11     H      2     1.0800     3     120.0      1     180.0
12     H      7     1.0800     3     120.0      2      90.0
13     H      7     1.0800     3     120.0      2     -90.0
14     H      8     1.0800     4     120.0      5      90.0
15     H      8     1.0800     4     120.0      5     -90.0
16     H      5     1.0800     4     120.0      6     180.0
17     H      6     1.0800     5     120.0      4     180.0
18     H      6     1.0800     5     120.0      4       0.0
```

6A, ϕ = 0°:

1	C						
2	C	1	1.4159				
3	C	2	1.4564	1	128.0		
4	C	3	1.5140	2	119.0	1	180.0
5	C	4	1.4564	3	119.0	2	180.0
6	C	5	1.4159	4	128.0	3	180.0
7	C	3	1.3885	2	119.0	1	0.0
8	C	4	1.3885	5	119.0	6	0.0
9	H	1	1.0800	2	120.0	3	0.0
10	H	2	1.0800	3	120.0	1	180.0
11	H	7	1.0800	3	120.0	2	0.0
12	H	7	1.0800	3	120.0	2	180.0
13	H	8	1.0800	4	120.0	5	0.0
14	H	8	1.0800	4	120.0	5	180.0
15	H	5	1.0800	4	120.0	6	180.0
16	H	6	1.0800	5	120.0	4	0.0
17	C	1	1.3948	2	125.0	3	180.0
18	C	6	1.3948	5	125.0	4	180.0
19	H	17	1.0800	1	120.0	2	180.0
20	H	17	1.0800	1	120.0	2	0.0
21	H	18	1.0800	6	120.0	5	180.0
22	H	18	1.0800	6	120.0	5	0.0

6A, ϕ = 20°:

1	C						
2	C	1	1.4158				
3	C	2	1.4545	1	127.0		
4	C	3	1.5118	2	119.0	1	180.0
5	C	4	1.4545	3	119.0	2	160.0
6	C	5	1.4158	4	127.0	3	180.0
7	C	3	1.3878	2	120.0	1	0.0
8	C	4	1.3878	5	120.0	6	0.0
9	H	1	1.0800	2	120.0	3	0.0
10	H	2	1.0800	3	120.0	1	180.0
11	H	7	1.0800	3	120.0	2	0.0
12	H	7	1.0800	3	120.0	2	180.0
13	H	8	1.0800	4	120.0	5	0.0
14	H	8	1.0800	4	120.0	5	180.0
15	H	5	1.0800	4	120.0	6	180.0
16	H	6	1.0800	5	120.0	4	0.0
17	C	1	1.3946	2	125.0	3	180.0
18	C	6	1.3946	5	125.0	4	180.0
19	H	17	1.0800	1	120.0	2	180.0
20	H	17	1.0800	1	120.0	2	0.0
21	H	18	1.0800	6	120.0	5	180.0
22	H	18	1.0800	6	120.0	5	0.0

6A, ϕ = 40°:

1	C						
2	C	1	1.4156				
3	C	2	1.4504	1	127.0		
4	C	3	1.5097	2	118.0	1	180.0
5	C	4	1.4504	3	118.0	2	140.0
6	C	5	1.4156	4	127.0	3	180.0
7	C	3	1.3860	2	122.0	1	0.0
8	C	4	1.3860	5	122.0	6	0.0
9	H	1	1.0800	2	120.0	3	0.0
10	H	2	1.0800	3	120.0	1	180.0

11	H	7	1.0800	3	120.0	2	0.0
12	H	7	1.0800	3	120.0	2	180.0
13	H	8	1.0800	4	120.0	5	0.0
14	H	8	1.0800	4	120.0	5	180.0
15	H	5	1.0800	4	120.0	6	180.0
16	H	6	1.0800	5	120.0	4	0.0
17	C	1	1.3946	2	125.0	3	180.0
18	C	6	1.3946	5	125.0	4	180.0
19	H	17	1.0800	1	120.0	2	180.0
20	H	17	1.0800	1	120.0	2	0.0
21	H	18	1.0800	6	120.0	5	180.0
22	H	18	1.0800	6	120.0	5	0.0

6A, $\phi = 60°$:

1	C						
2	C	1	1.4157				
3	C	2	1.4474	1	126.0		
4	C	3	1.5106	2	117.0	1	180.0
5	C	4	1.4474	3	117.0	2	120.0
6	C	5	1.4157	4	126.0	3	180.0
7	C	3	1.3835	2	124.0	1	0.0
8	C	4	1.3835	5	124.0	6	0.0
9	H	1	1.0800	2	120.0	3	0.0
10	H	2	1.0800	3	120.0	1	180.0
11	H	7	1.0800	3	120.0	2	0.0
12	H	7	1.0800	3	120.0	2	180.0
13	H	8	1.0800	4	120.0	5	0.0
14	H	8	1.0800	4	120.0	5	180.0
15	H	5	1.0800	4	120.0	6	180.0
16	H	6	1.0800	5	120.0	4	0.0
17	C	1	1.3942	2	125.0	3	180.0
18	C	6	1.3942	5	125.0	4	180.0
19	H	17	1.0800	1	120.0	2	180.0
20	H	17	1.0800	1	120.0	2	0.0
21	H	18	1.0800	6	120.0	5	180.0
22	H	18	1.0800	6	120.0	5	0.0

6A, $\phi = 80°$:

1	C						
2	C	1	1.4163				
3	C	2	1.4446	1	126.0		
4	C	3	1.5096	2	117.0	1	180.0
5	C	4	1.4446	3	117.0	2	100.0
6	C	5	1.4163	4	126.0	3	180.0
7	C	3	1.3836	2	125.0	1	0.0
8	C	4	1.3836	5	125.0	6	0.0
9	H	1	1.0800	2	120.0	3	0.0
10	H	2	1.0800	3	120.0	1	180.0
11	H	7	1.0800	3	120.0	2	0.0
12	H	7	1.0800	3	120.0	2	180.0
13	H	8	1.0800	4	120.0	5	0.0
14	H	8	1.0800	4	120.0	5	180.0
15	H	5	1.0800	4	120.0	6	180.0
16	H	6	1.0800	5	120.0	4	0.0
17	C	1	1.3935	2	125.0	3	180.0
18	C	6	1.3935	5	125.0	4	180.0
19	H	17	1.0800	1	120.0	2	180.0

```
20    H    17    1.0800    1    120.0    2      0.0
21    H    18    1.0800    6    120.0    5    180.0
22    H    18    1.0800    6    120.0    5      0.0
```

6A, ϕ = 100°:

```
 1    C
 2    C     1    1.4166
 3    C     2    1.4436    1    126.0
 4    C     3    1.5100    2    117.0    1    180.0
 5    C     4    1.4436    3    117.0    2     80.0
 6    C     5    1.4166    4    126.0    3    180.0
 7    C     3    1.3847    2    125.0    1      0.0
 8    C     4    1.3847    5    125.0    6      0.0
 9    H     1    1.0800    2    120.0    3      0.0
10    H     2    1.0800    3    120.0    1    180.0
11    H     7    1.0800    3    120.0    2      0.0
12    H     7    1.0800    3    120.0    2    180.0
13    H     8    1.0800    4    120.0    5      0.0
14    H     8    1.0800    4    120.0    5    180.0
15    H     5    1.0800    4    120.0    6    180.0
16    H     6    1.0800    5    120.0    4      0.0
17    C     1    1.3932    2    125.0    3    180.0
18    C     6    1.3932    5    125.0    4    180.0
19    H    17    1.0800    1    120.0    2    180.0
20    H    17    1.0800    1    120.0    2      0.0
21    H    18    1.0800    6    120.0    5    180.0
22    H    18    1.0800    6    120.0    5      0.0
```

6A, ϕ = 120°:

```
 1    C
 2    C     1    1.4168
 3    C     2    1.4439    1    126.0
 4    C     3    1.5094    2    118.0    1    180.0
 5    C     4    1.4439    3    118.0    2     60.0
 6    C     5    1.4168    4    126.0    3    180.0
 7    C     3    1.3866    2    124.0    1      0.0
 8    C     4    1.3866    5    124.0    6      0.0
 9    H     1    1.0800    2    120.0    3      0.0
10    H     2    1.0800    3    120.0    1    180.0
11    H     7    1.0800    3    120.0    2      0.0
12    H     7    1.0800    3    120.0    2    180.0
13    H     8    1.0800    4    120.0    5      0.0
14    H     8    1.0800    4    120.0    5    180.0
15    H     5    1.0800    4    120.0    6    180.0
16    H     6    1.0800    5    120.0    4      0.0
17    C     1    1.3931    2    125.0    3    180.0
18    C     6    1.3931    5    125.0    4    180.0
19    H    17    1.0800    1    120.0    2    180.0
20    H    17    1.0800    1    120.0    2      0.0
21    H    18    1.0800    6    120.0    5    180.0
22    H    18    1.0800    6    120.0    5      0.0
```

6B, $\phi = 0°$:

1	C						
2	C	1	1.4194				
3	C	2	1.4593	1	134.0		
4	C	3	1.4983	2	128.0	1	0.0
5	C	4	1.4593	3	128.0	2	180.0
6	C	5	1.4194	4	134.0	3	0.0
7	C	3	1.3959	2	109.0	1	180.0
8	C	4	1.3959	5	109.0	6	180.0
9	H	1	1.0800	2	120.0	3	0.0
10	H	2	1.0800	3	120.0	1	180.0
11	H	7	1.0800	3	120.0	2	0.0
12	H	7	1.0800	3	120.0	2	180.0
13	H	8	1.0800	4	120.0	5	0.0
14	H	8	1.0800	4	120.0	5	180.0
15	H	5	1.0800	4	120.0	6	180.0
16	H	6	1.0800	5	120.0	4	0.0
17	C	1	1.3935	2	125.0	3	180.0
18	C	6	1.3935	5	125.0	4	180.0
19	H	17	1.0800	1	120.0	2	180.0
20	H	17	1.0800	1	120.0	2	0.0
21	H	18	1.0800	6	120.0	5	180.0
22	H	18	1.0800	6	120.0	5	0.0

6B, $\phi = 20°$:

1	C						
2	C	1	1.4186				
3	C	2	1.4572	1	132.0		
4	C	3	1.4972	2	127.0	1	0.0
5	C	4	1.4572	3	127.0	2	160.0
6	C	5	1.4186	4	132.0	3	0.0
7	C	3	1.3944	2	110.0	1	180.0
8	C	4	1.3944	5	110.0	6	180.0
9	H	1	1.0800	2	120.0	3	0.0
10	H	2	1.0800	3	120.0	1	180.0
11	H	7	1.0800	3	120.0	2	0.0
12	H	7	1.0800	3	120.0	2	180.0
13	H	8	1.0800	4	120.0	5	0.0
14	H	8	1.0800	4	120.0	5	180.0
15	H	5	1.0800	4	120.0	6	180.0
16	H	6	1.0800	5	120.0	4	0.0
17	C	1	1.3935	2	125.0	3	180.0
18	C	6	1.3935	5	125.0	4	180.0
19	H	17	1.0800	1	120.0	2	180.0
20	H	17	1.0800	1	120.0	2	0.0
21	H	18	1.0800	6	120.0	5	180.0
22	H	18	1.0800	6	120.0	5	0.0

6B, $\phi = 40°$:

1	C						
2	C	1	1.4176				
3	C	2	1.4517	1	129.0		
4	C	3	1.4964	2	125.0	1	0.0
5	C	4	1.4517	3	125.0	2	140.0
6	C	5	1.4176	4	129.0	3	0.0
7	C	3	1.3914	2	114.0	1	180.0
8	C	4	1.3914	5	114.0	6	180.0
9	H	1	1.0800	2	120.0	3	0.0
10	H	2	1.0800	3	120.0	1	180.0

11	H	7	1.0800	3	120.0	2	0.0
12	H	7	1.0800	3	120.0	2	180.0
13	H	8	1.0800	4	120.0	5	0.0
14	H	8	1.0800	4	120.0	5	180.0
15	H	5	1.0800	4	120.0	6	180.0
16	H	6	1.0800	5	120.0	4	0.0
17	C	1	1.3932	2	125.0	3	180.0
18	C	6	1.3932	5	125.0	4	180.0
19	H	17	1.0800	1	120.0	2	180.0
20	H	17	1.0800	1	120.0	2	0.0
21	H	18	1.0800	6	120.0	5	180.0
22	H	18	1.0800	6	120.0	5	0.0

6B, $\phi = 60°$:

1	C						
2	C	1	1.4172				
3	C	2	1.4475	1	127.0		
4	C	3	1.4977	2	124.0	1	0.0
5	C	4	1.4475	3	124.0	2	120.0
6	C	5	1.4172	4	127.0	3	0.0
7	C	3	1.3885	2	117.0	1	180.0
8	C	4	1.3885	5	117.0	6	180.0
9	H	1	1.0800	2	120.0	3	0.0
10	H	2	1.0800	3	120.0	1	180.0
11	H	7	1.0800	3	120.0	2	0.0
12	H	7	1.0800	3	120.0	2	180.0
13	H	8	1.0800	4	120.0	5	0.0
14	H	8	1.0800	4	120.0	5	180.0
15	H	5	1.0800	4	120.0	6	180.0
16	H	6	1.0800	5	120.0	4	0.0
17	C	1	1.3929	2	124.0	3	180.0
18	C	6	1.3929	5	124.0	4	180.0
19	H	17	1.0800	1	120.0	2	180.0
20	H	17	1.0800	1	120.0	2	0.0
21	H	18	1.0800	6	120.0	5	180.0
22	H	18	1.0800	6	120.0	5	0.0

6B, $\phi = 80°$:

1	C						
2	C	1	1.4172				
3	C	2	1.4443	1	126.0		
4	C	3	1.4978	2	122.0	1	0.0
5	C	4	1.4443	3	122.0	2	100.0
6	C	5	1.4172	4	126.0	3	0.0
7	C	3	1.3880	2	119.0	1	180.0
8	C	4	1.3880	5	119.0	6	180.0
9	H	1	1.0800	2	120.0	3	0.0
10	H	2	1.0800	3	120.0	1	180.0
11	H	7	1.0800	3	120.0	2	0.0
12	H	7	1.0800	3	120.0	2	180.0
13	H	8	1.0800	4	120.0	5	0.0
14	H	8	1.0800	4	120.0	5	180.0
15	H	5	1.0800	4	120.0	6	180.0
16	H	6	1.0800	5	120.0	4	0.0
17	C	1	1.3921	2	124.0	3	180.0
18	C	6	1.3921	5	124.0	4	180.0
19	H	17	1.0800	1	120.0	2	180.0

20	H	17	1.0800	1	120.0	2	0.0
21	H	18	1.0800	6	120.0	5	180.0
22	H	18	1.0800	6	120.0	5	0.0

6B, ϕ = 100°:

1	C						
2	C	1	1.4183				
3	C	2	1.4424	1	126.0		
4	C	3	1.4980	2	122.0	1	0.0
5	C	4	1.4424	3	122.0	2	80.0
6	C	5	1.4183	4	126.0	3	0.0
7	C	3	1.3895	2	119.0	1	180.0
8	C	4	1.3895	5	119.0	6	180.0
9	H	1	1.0800	2	120.0	3	0.0
10	H	2	1.0800	3	120.0	1	180.0
11	H	7	1.0800	3	120.0	2	0.0
12	H	7	1.0800	3	120.0	2	180.0
13	H	8	1.0800	4	120.0	5	0.0
14	H	8	1.0800	4	120.0	5	180.0
15	H	5	1.0800	4	120.0	6	180.0
16	H	6	1.0800	5	120.0	4	0.0
17	C	1	1.3912	2	124.0	3	180.0
18	C	6	1.3912	5	124.0	4	180.0
19	H	17	1.0800	1	120.0	2	180.0
20	H	17	1.0800	1	120.0	2	0.0
21	H	18	1.0800	6	120.0	5	180.0
22	H	18	1.0800	6	120.0	5	0.0

6B, ϕ = 120°:

1	C						
2	C	1	1.4196				
3	C	2	1.4414	1	128.0		
4	C	3	1.4984	2	124.0	1	0.0
5	C	4	1.4414	3	124.0	2	60.0
6	C	5	1.4196	4	128.0	3	0.0
7	C	3	1.3933	2	117.0	1	180.0
8	C	4	1.3933	5	117.0	6	180.0
9	H	1	1.0800	2	120.0	3	0.0
10	H	2	1.0800	3	120.0	1	180.0
11	H	7	1.0800	3	120.0	2	0.0
12	H	7	1.0800	3	120.0	2	180.0
13	H	8	1.0800	4	120.0	5	0.0
14	H	8	1.0800	4	120.0	5	180.0
15	H	5	1.0800	4	120.0	6	180.0
16	H	6	1.0800	5	120.0	4	0.0
17	C	1	1.3906	2	124.0	3	180.0
18	C	6	1.3906	5	124.0	4	180.0
19	H	17	1.0800	1	120.0	2	180.0
20	H	17	1.0800	1	120.0	2	0.0
21	H	18	1.0800	6	120.0	5	180.0
22	H	18	1.0800	6	120.0	5	0.0

6C, ϕ = 0°:

1	C						
2	C	1	1.4469				
3	C	2	1.3838	1	126.0		
4	C	3	1.4874	2	125.0	1	180.0
5	C	4	1.3838	3	125.0	2	180.0
6	C	5	1.4469	4	126.0	3	180.0
7	C	3	1.4640	2	119.0	1	0.0
8	C	4	1.4640	5	119.0	6	0.0
9	H	1	1.0800	2	120.0	3	0.0
10	H	2	1.0800	3	120.0	1	180.0
11	H	7	1.0800	3	120.0	2	90.0
12	H	7	1.0800	3	120.0	2	-90.0
13	H	8	1.0800	4	120.0	5	90.0
14	H	8	1.0800	4	120.0	5	-90.0
15	H	5	1.0800	4	120.0	6	180.0
16	H	6	1.0800	5	120.0	4	0.0
17	C	1	1.3693	2	124.0	3	180.0
18	C	6	1.3693	5	124.0	4	180.0
19	H	17	1.0800	1	120.0	2	180.0
20	H	17	1.0800	1	120.0	2	0.0
21	H	18	1.0800	6	120.0	5	180.0
22	H	18	1.0800	6	120.0	5	0.0

6C, ϕ = 20°:

1	C						
2	C	1	1.4427				
3	C	2	1.3890	1	125.0		
4	C	3	1.4837	2	125.0	1	180.0
5	C	4	1.3890	3	125.0	2	160.0
6	C	5	1.4427	4	125.0	3	180.0
7	C	3	1.4610	2	120.0	1	0.0
8	C	4	1.4610	5	120.0	6	0.0
9	H	1	1.0800	2	120.0	3	0.0
10	H	2	1.0800	3	120.0	1	180.0
11	H	7	1.0800	3	120.0	2	90.0
12	H	7	1.0800	3	120.0	2	-90.0
13	H	8	1.0800	4	120.0	5	90.0
14	H	8	1.0800	4	120.0	5	-90.0
15	H	5	1.0800	4	120.0	6	180.0
16	H	6	1.0800	5	120.0	4	0.0
17	C	1	1.3729	2	124.0	3	180.0
18	C	6	1.3729	5	124.0	4	180.0
19	H	17	1.0800	1	120.0	2	180.0
20	H	17	1.0800	1	120.0	2	0.0
21	H	18	1.0800	6	120.0	5	180.0
22	H	18	1.0800	6	120.0	5	0.0

6C, ϕ = 40°:

1	C						
2	C	1	1.4433				
3	C	2	1.3869	1	125.0		
4	C	3	1.4877	2	124.0	1	180.0
5	C	4	1.3869	3	124.0	2	140.0
6	C	5	1.4433	4	125.0	3	180.0
7	C	3	1.4592	2	122.0	1	0.0
8	C	4	1.4592	5	122.0	6	0.0
9	H	1	1.0800	2	120.0	3	0.0
10	H	2	1.0800	3	120.0	1	180.0

11	H	7	1.0800	3	120.0	2	90.0
12	H	7	1.0800	3	120.0	2	-90.0
13	H	8	1.0800	4	120.0	5	90.0
14	H	8	1.0800	4	120.0	5	-90.0
15	H	5	1.0800	4	120.0	6	180.0
16	H	6	1.0800	5	120.0	4	0.0
17	C	1	1.3722	2	124.0	3	180.0
18	C	6	1.3722	5	124.0	4	180.0
19	H	17	1.0800	1	120.0	2	180.0
20	H	17	1.0800	1	120.0	2	0.0
21	H	18	1.0800	6	120.0	5	180.0
22	H	18	1.0800	6	120.0	5	0.0

6C, ϕ = 60°:

1	C						
2	C	1	1.4436				
3	C	2	1.3847	1	125.0		
4	C	3	1.4921	2	124.0	1	180.0
5	C	4	1.3847	3	124.0	2	120.0
6	C	5	1.4436	4	125.0	3	180.0
7	C	3	1.4561	2	124.0	1	0.0
8	C	4	1.4561	5	124.0	6	0.0
9	H	1	1.0800	2	120.0	3	0.0
10	H	2	1.0800	3	120.0	1	180.0
11	H	7	1.0800	3	120.0	2	90.0
12	H	7	1.0800	3	120.0	2	-90.0
13	H	8	1.0800	4	120.0	5	90.0
14	H	8	1.0800	4	120.0	5	-90.0
15	H	5	1.0800	4	120.0	6	180.0
16	H	6	1.0800	5	120.0	4	0.0
17	C	1	1.3718	2	124.0	3	180.0
18	C	6	1.3718	5	124.0	4	180.0
19	H	17	1.0800	1	120.0	2	180.0
20	H	17	1.0800	1	120.0	2	0.0
21	H	18	1.0800	6	120.0	5	180.0
22	H	18	1.0800	6	120.0	5	0.0

6C, ϕ = 80°:

1	C						
2	C	1	1.4444				
3	C	2	1.3835	1	125.0		
4	C	3	1.4937	2	122.0	1	180.0
5	C	4	1.3835	3	122.0	2	100.0
6	C	5	1.4444	4	125.0	3	180.0
7	C	3	1.4537	2	125.0	1	0.0
8	C	4	1.4537	5	125.0	6	0.0
9	H	1	1.0800	2	120.0	3	0.0
10	H	2	1.0800	3	120.0	1	180.0
11	H	7	1.0800	3	120.0	2	90.0
12	H	7	1.0800	3	120.0	2	-90.0
13	H	8	1.0800	4	120.0	5	90.0
14	H	8	1.0800	4	120.0	5	-90.0
15	H	5	1.0800	4	120.0	6	180.0
16	H	6	1.0800	5	120.0	4	0.0
17	C	1	1.3714	2	124.0	3	180.0
18	C	6	1.3714	5	124.0	4	180.0
19	H	17	1.0800	1	120.0	2	180.0

20	H	17	1.0800	1	120.0	2	0.0
21	H	18	1.0800	6	120.0	5	180.0
22	H	18	1.0800	6	120.0	5	0.0

6C, ϕ = 100°:

1	C						
2	C	1	1.4455				
3	C	2	1.3839	1	125.0		
4	C	3	1.4942	2	121.0	1	180.0
5	C	4	1.3839	3	121.0	2	80.0
6	C	5	1.4455	4	125.0	3	180.0
7	C	3	1.4531	2	124.0	1	0.0
8	C	4	1.4531	5	124.0	6	0.0
9	H	1	1.0800	2	120.0	3	0.0
10	H	2	1.0800	3	120.0	1	180.0
11	H	7	1.0800	3	120.0	2	90.0
12	H	7	1.0800	3	120.0	2	-90.0
13	H	8	1.0800	4	120.0	5	90.0
14	H	8	1.0800	4	120.0	5	-90.0
15	H	5	1.0800	4	120.0	6	180.0
16	H	6	1.0800	5	120.0	4	0.0
17	C	1	1.3708	2	124.0	3	180.0
18	C	6	1.3708	5	124.0	4	180.0
19	H	17	1.0800	1	120.0	2	180.0
20	H	17	1.0800	1	120.0	2	0.0
21	H	18	1.0800	6	120.0	5	180.0
22	H	18	1.0800	6	120.0	5	0.0

6C, ϕ = 120°:

1	C						
2	C	1	1.4467				
3	C	2	1.3858	1	125.0		
4	C	3	1.4922	2	121.0	1	180.0
5	C	4	1.3858	3	121.0	2	60.0
6	C	5	1.4467	4	125.0	3	180.0
7	C	3	1.4544	2	122.0	1	0.0
8	C	4	1.4544	5	122.0	6	0.0
9	H	1	1.0800	2	120.0	3	0.0
10	H	2	1.0800	3	120.0	1	180.0
11	H	7	1.0800	3	120.0	2	90.0
12	H	7	1.0800	3	120.0	2	-90.0
13	H	8	1.0800	4	120.0	5	90.0
14	H	8	1.0800	4	120.0	5	-90.0
15	H	5	1.0800	4	120.0	6	180.0
16	H	6	1.0800	5	120.0	4	0.0
17	C	1	1.3701	2	124.0	3	180.0
18	C	6	1.3701	5	124.0	4	180.0
19	H	17	1.0800	1	120.0	2	180.0
20	H	17	1.0800	1	120.0	2	0.0
21	H	18	1.0800	6	120.0	5	180.0
22	H	18	1.0800	6	120.0	5	0.0

6D, ϕ = 0°:

1	C						
2	C	1	1.4478				
3	C	2	1.3831	1	129.0		
4	C	3	1.4808	2	129.0	1	0.0
5	C	4	1.3831	3	129.0	2	180.0
6	C	5	1.4478	4	129.0	3	0.0
7	C	3	1.4695	2	113.0	1	180.0
8	C	4	1.4695	5	113.0	6	180.0
9	H	1	1.0800	2	120.0	3	0.0
10	H	2	1.0800	3	120.0	1	180.0
11	H	7	1.0800	3	120.0	2	90.0
12	H	7	1.0800	3	120.0	2	-90.0
13	H	8	1.0800	4	120.0	5	90.0
14	H	8	1.0800	4	120.0	5	-90.0
15	H	5	1.0800	4	120.0	6	180.0
16	H	6	1.0800	5	120.0	4	0.0
17	C	1	1.3692	2	124.0	3	180.0
18	C	6	1.3692	5	124.0	4	180.0
19	H	17	1.0800	1	120.0	2	180.0
20	H	17	1.0800	1	120.0	2	0.0
21	H	18	1.0800	6	120.0	5	180.0
22	H	18	1.0800	6	120.0	5	0.0

6D, ϕ = 20°:

1	C						
2	C	1	1.4468				
3	C	2	1.3847	1	129.0		
4	C	3	1.4803	2	130.0	1	0.0
5	C	4	1.3847	3	130.0	2	160.0
6	C	5	1.4468	4	129.0	3	0.0
7	C	3	1.4691	2	113.0	1	180.0
8	C	4	1.4691	5	113.0	6	180.0
9	H	1	1.0800	2	120.0	3	0.0
10	H	2	1.0800	3	120.0	1	180.0
11	H	7	1.0800	3	120.0	2	90.0
12	H	7	1.0800	3	120.0	2	-90.0
13	H	8	1.0800	4	120.0	5	90.0
14	H	8	1.0800	4	120.0	5	-90.0
15	H	5	1.0800	4	120.0	6	180.0
16	H	6	1.0800	5	120.0	4	0.0
17	C	1	1.3700	2	124.0	3	180.0
18	C	6	1.3700	5	124.0	4	180.0
19	H	17	1.0800	1	120.0	2	180.0
20	H	17	1.0800	1	120.0	2	0.0
21	H	18	1.0800	6	120.0	5	180.0
22	H	18	1.0800	6	120.0	5	0.0

6D, ϕ = 40°:

1	C						
2	C	1	1.4454				
3	C	2	1.3851	1	129.0		
4	C	3	1.4819	2	130.0	1	0.0
5	C	4	1.3851	3	130.0	2	140.0
6	C	5	1.4454	4	129.0	3	0.0
7	C	3	1.4676	2	115.0	1	180.0
8	C	4	1.4676	5	115.0	6	180.0
9	H	1	1.0800	2	120.0	3	0.0
10	H	2	1.0800	3	120.0	1	180.0

11	H	7	1.0800	3	120.0	2	90.0
12	H	7	1.0800	3	120.0	2	-90.0
13	H	8	1.0800	4	120.0	5	90.0
14	H	8	1.0800	4	120.0	5	-90.0
15	H	5	1.0800	4	120.0	6	180.0
16	H	6	1.0800	5	120.0	4	0.0
17	C	1	1.3709	2	124.0	3	180.0
18	C	6	1.3709	5	124.0	4	180.0
19	H	17	1.0800	1	120.0	2	180.0
20	H	17	1.0800	1	120.0	2	0.0
21	H	18	1.0800	6	120.0	5	180.0
22	H	18	1.0800	6	120.0	5	0.0

6D, $\phi = 60°$:

1	C						
2	C	1	1.4440				
3	C	2	1.3839	1	127.0		
4	C	3	1.4851	2	129.0	1	0.0
5	C	4	1.3839	3	129.0	2	120.0
6	C	5	1.4440	4	127.0	3	0.0
7	C	3	1.4632	2	120.0	1	180.0
8	C	4	1.4632	5	120.0	6	180.0
9	H	1	1.0800	2	120.0	3	0.0
10	H	2	1.0800	3	120.0	1	180.0
11	H	7	1.0800	3	120.0	2	90.0
12	H	7	1.0800	3	120.0	2	-90.0
13	H	8	1.0800	4	120.0	5	90.0
14	H	8	1.0800	4	120.0	5	-90.0
15	H	5	1.0800	4	120.0	6	180.0
16	H	6	1.0800	5	120.0	4	0.0
17	C	1	1.3716	2	124.0	3	180.0
18	C	6	1.3716	5	124.0	4	180.0
19	H	17	1.0800	1	120.0	2	180.0
20	H	17	1.0800	1	120.0	2	0.0
21	H	18	1.0800	6	120.0	5	180.0
22	H	18	1.0800	6	120.0	5	0.0

6D, $\phi = 80°$:

1	C						
2	C	1	1.4428				
3	C	2	1.3834	1	126.0		
4	C	3	1.4879	2	127.0	1	0.0
5	C	4	1.3834	3	127.0	2	100.0
6	C	5	1.4428	4	126.0	3	0.0
7	C	3	1.4584	2	123.0	1	180.0
8	C	4	1.4584	5	123.0	6	180.0
9	H	1	1.0800	2	120.0	3	0.0
10	H	2	1.0800	3	120.0	1	180.0
11	H	7	1.0800	3	120.0	2	90.0
12	H	7	1.0800	3	120.0	2	-90.0
13	H	8	1.0800	4	120.0	5	90.0
14	H	8	1.0800	4	120.0	5	-90.0
15	H	5	1.0800	4	120.0	6	180.0
16	H	6	1.0800	5	120.0	4	0.0
17	C	1	1.3719	2	124.0	3	180.0
18	C	6	1.3719	5	124.0	4	180.0
19	H	17	1.0800	1	120.0	2	180.0

20	H	17	1.0800	1	120.0	2	0.0
21	H	18	1.0800	6	120.0	5	180.0
22	H	18	1.0800	6	120.0	5	0.0

6D, ϕ = 100°:

1	C						
2	C	1	1.4434				
3	C	2	1.3853	1	126.0		
4	C	3	1.4880	2	125.0	1	0.0
5	C	4	1.3853	3	125.0	2	80.0
6	C	5	1.4434	4	126.0	3	0.0
7	C	3	1.4577	2	121.0	1	180.0
8	C	4	1.4577	5	121.0	6	180.0
9	H	1	1.0800	2	120.0	3	0.0
10	H	2	1.0800	3	120.0	1	180.0
11	H	7	1.0800	3	120.0	2	90.0
12	H	7	1.0800	3	120.0	2	-90.0
13	H	8	1.0800	4	120.0	5	90.0
14	H	8	1.0800	4	120.0	5	-90.0
15	H	5	1.0800	4	120.0	6	180.0
16	H	6	1.0800	5	120.0	4	0.0
17	C	1	1.3712	2	124.0	3	180.0
18	C	6	1.3712	5	124.0	4	180.0
19	H	17	1.0800	1	120.0	2	180.0
20	H	17	1.0800	1	120.0	2	0.0
21	H	18	1.0800	6	120.0	5	180.0
22	H	18	1.0800	6	120.0	5	0.0

6D, ϕ = 120°:

1	C						
2	C	1	1.4437				
3	C	2	1.3882	1	127.0		
4	C	3	1.4832	2	127.0	1	0.0
5	C	4	1.3882	3	127.0	2	180.0
6	C	5	1.4437	4	127.0	3	0.0
7	C	3	1.4612	2	118.0	1	180.0
8	C	4	1.4612	5	118.0	6	180.0
9	H	1	1.0800	2	120.0	3	0.0
10	H	2	1.0800	3	120.0	1	180.0
11	H	7	1.0800	3	120.0	2	90.0
12	H	7	1.0800	3	120.0	2	-90.0
13	H	8	1.0800	4	120.0	5	90.0
14	H	8	1.0800	4	120.0	5	-90.0
15	H	5	1.0800	4	120.0	6	180.0
16	H	6	1.0800	5	120.0	4	0.0
17	C	1	1.3712	2	124.0	3	180.0
18	C	6	1.3712	5	124.0	4	180.0
19	H	17	1.0800	1	120.0	2	180.0
20	H	17	1.0800	1	120.0	2	0.0
21	H	18	1.0800	6	120.0	5	180.0
22	H	18	1.0800	6	120.0	5	0.0

3A, ϕ = 0°:

1	C						
2	C	1	1.3527				
3	C	2	1.5739	1	120.0		
4	C	3	1.6557	2	120.0	1	180.0
5	C	4	1.5739	3	120.0	2	180.0
6	C	5	1.3527	4	120.0	3	180.0
7	C	3	1.4728	2	120.0	1	0.0
8	C	4	1.4728	5	120.0	6	0.0
9	H	1	1.0800	2	120.0	3	180.0
10	H	1	1.0800	2	120.0	3	0.0
11	H	2	1.0800	3	120.0	1	180.0
12	C	7	1.5400	3	120.0	2	0.0
13	C	7	1.5400	3	120.0	2	180.0
14	C	8	1.5400	4	120.0	5	0.0
15	C	8	1.5400	4	120.0	5	180.0
16	H	5	1.0800	4	120.0	6	180.0
17	H	6	1.0800	5	120.0	4	180.0
18	H	6	1.0800	5	120.0	4	0.0
19	H	12	1.0800	7	120.0	3	180.0
20	H	12	1.0800	7	120.0	3	-60.0
21	H	12	1.0800	7	120.0	3	60.0
22	H	13	1.0800	7	120.0	3	180.0
23	H	13	1.0800	7	120.0	3	-60.0
24	H	13	1.0800	7	120.0	3	60.0
25	H	14	1.0800	8	120.0	4	180.0
26	H	14	1.0800	8	120.0	4	60.0
27	H	14	1.0800	8	120.0	4	-60.0
28	H	15	1.0800	8	120.0	4	180.0
29	H	15	1.0800	8	120.0	4	60.0
30	H	15	1.0800	8	120.0	4	-60.0

3A, ϕ = 20°:

1	C						
2	C	1	1.3526				
3	C	2	1.5723	1	120.0		
4	C	3	1.6229	2	120.0	1	180.0
5	C	4	1.5723	3	120.0	2	160.0
6	C	5	1.3526	4	120.0	3	180.0
7	C	3	1.4744	2	120.0	1	0.0
8	C	4	1.4744	5	120.0	6	0.0
9	H	1	1.0800	2	120.0	3	180.0
10	H	1	1.0800	2	120.0	3	0.0
11	H	2	1.0800	3	120.0	1	180.0
12	C	7	1.5400	3	120.0	2	0.0
13	C	7	1.5400	3	120.0	2	180.0
14	C	8	1.5400	4	120.0	5	0.0
15	C	8	1.5400	4	120.0	5	180.0
16	H	5	1.0800	4	120.0	6	180.0
17	H	6	1.0800	5	120.0	4	180.0
18	H	6	1.0800	5	120.0	4	0.0
19	H	12	1.0800	7	120.0	3	180.0
20	H	12	1.0800	7	120.0	3	-60.0
21	H	12	1.0800	7	120.0	3	60.0
22	H	13	1.0800	7	120.0	3	180.0
23	H	13	1.0800	7	120.0	3	-60.0
24	H	13	1.0800	7	120.0	3	60.0
25	H	14	1.0800	8	120.0	4	180.0
26	H	14	1.0800	8	120.0	4	60.0

27	H	14	1.0800	8	120.0	4	-60.0
28	H	15	1.0800	8	120.0	4	180.0
29	H	15	1.0800	8	120.0	4	60.0
30	H	15	1.0800	8	120.0	4	-60.0

3A, $\phi = 40°$:

1	C						
2	C	1	1.3524				
3	C	2	1.5802	1	120.0		
4	C	3	1.5198	2	120.0	1	180.0
5	C	4	1.5802	3	120.0	2	140.0
6	C	5	1.3524	4	120.0	3	180.0
7	C	3	1.4579	2	120.0	1	0.0
8	C	4	1.4579	5	120.0	6	0.0
9	H	1	1.0800	2	120.0	3	180.0
10	H	1	1.0800	2	120.0	3	0.0
11	H	2	1.0800	3	120.0	1	180.0
12	C	7	1.5400	3	120.0	2	0.0
13	C	7	1.5400	3	120.0	2	180.0
14	C	8	1.5400	4	120.0	5	0.0
15	C	8	1.5400	4	120.0	5	180.0
16	H	5	1.0800	4	120.0	6	180.0
17	H	6	1.0800	5	120.0	4	180.0
18	H	6	1.0800	5	120.0	4	0.0
19	H	12	1.0800	7	120.0	3	180.0
20	H	12	1.0800	7	120.0	3	-60.0
21	H	12	1.0800	7	120.0	3	60.0
22	H	13	1.0800	7	120.0	3	180.0
23	H	13	1.0800	7	120.0	3	-60.0
24	H	13	1.0800	7	120.0	3	60.0
25	H	14	1.0800	8	120.0	4	180.0
26	H	14	1.0800	8	120.0	4	60.0
27	H	14	1.0800	8	120.0	4	-60.0
28	H	15	1.0800	8	120.0	4	180.0
29	H	15	1.0800	8	120.0	4	60.0
30	H	15	1.0800	8	120.0	4	-60.0

3A, $\phi = 60°$:

1	C						
2	C	1	1.3525				
3	C	2	1.5842	1	120.0		
4	C	3	1.4786	2	120.0	1	180.0
5	C	4	1.5842	3	120.0	2	120.0
6	C	5	1.3525	4	120.0	3	180.0
7	C	3	1.4406	2	120.0	1	0.0
8	C	4	1.4406	5	120.0	6	0.0
9	H	1	1.0800	2	120.0	3	180.0
10	H	1	1.0800	2	120.0	3	0.0
11	H	2	1.0800	3	120.0	1	180.0
12	C	7	1.5400	3	120.0	2	0.0
13	C	7	1.5400	3	120.0	2	180.0
14	C	8	1.5400	4	120.0	5	0.0
15	C	8	1.5400	4	120.0	5	180.0
16	H	5	1.0800	4	120.0	6	180.0
17	H	6	1.0800	5	120.0	4	180.0
18	H	6	1.0800	5	120.0	4	0.0
19	H	12	1.0800	7	120.0	3	180.0
20	H	12	1.0800	7	120.0	3	-60.0
21	H	12	1.0800	7	120.0	3	60.0

```
22    H    13    1.0800    7    120.0    3    180.0
23    H    13    1.0800    7    120.0    3    -60.0
24    H    13    1.0800    7    120.0    3     60.0
25    H    14    1.0800    8    120.0    4    180.0
26    H    14    1.0800    8    120.0    4     60.0
27    H    14    1.0800    8    120.0    4    -60.0
28    H    15    1.0800    8    120.0    4    180.0
29    H    15    1.0800    8    120.0    4     60.0
30    H    15    1.0800    8    120.0    4    -60.0
```

3A, $\phi = 80°$:

```
 1    C
 2    C     1    1.3525
 3    C     2    1.5829    1    120.0
 4    C     3    1.4716    2    120.0    1    180.0
 5    C     4    1.5829    3    120.0    2    100.0
 6    C     5    1.3526    4    120.0    3    180.0
 7    C     3    1.4364    2    120.0    1      0.0
 8    C     4    1.4364    5    120.0    6      0.0
 9    H     1    1.0800    2    120.0    3    180.0
10    H     1    1.0800    2    120.0    3      0.0
11    H     2    1.0800    3    120.0    1    180.0
12    C     7    1.5400    3    120.0    2      0.0
13    C     7    1.5400    3    120.0    2    180.0
14    C     8    1.5400    4    120.0    5      0.0
15    C     8    1.5400    4    120.0    5    180.0
16    H     5    1.0800    4    120.0    6    180.0
17    H     6    1.0800    5    120.0    4    180.0
18    H     6    1.0800    5    120.0    4      0.0
19    H    12    1.0800    7    120.0    3    180.0
20    H    12    1.0800    7    120.0    3    -60.0
21    H    12    1.0800    7    120.0    3     60.0
22    H    13    1.0800    7    120.0    3    180.0
23    H    13    1.0800    7    120.0    3    -60.0
24    H    13    1.0800    7    120.0    3     60.0
25    H    14    1.0800    8    120.0    4    180.0
26    H    14    1.0800    8    120.0    4     60.0
27    H    14    1.0800    8    120.0    4    -60.0
28    H    15    1.0800    8    120.0    4    180.0
29    H    15    1.0800    8    120.0    4     60.0
30    H    15    1.0800    8    120.0    4    -60.0
```

3A, $\phi = 100°$:

```
 1    C
 2    C     1    1.3526
 3    C     2    1.5800    1    120.0
 4    C     3    1.4728    2    120.0    1    180.0
 5    C     4    1.5800    3    120.0    2     80.0
 6    C     5    1.3526    4    120.0    3    180.0
 7    C     3    1.4406    2    120.0    1      0.0
 8    C     4    1.4406    5    120.0    6      0.0
 9    H     1    1.0800    2    120.0    3    180.0
10    H     1    1.0800    2    120.0    3      0.0
11    H     2    1.0800    3    120.0    1    180.0
12    C     7    1.5400    3    120.0    2      0.0
13    C     7    1.5400    3    120.0    2    180.0
14    C     8    1.5400    4    120.0    5      0.0
15    C     8    1.5400    4    120.0    5    180.0
16    H     5    1.0800    4    120.0    6    180.0
```

17	H	6	1.0800	5	120.0	4	180.0
18	H	6	1.0800	5	120.0	4	0.0
19	H	12	1.0800	7	120.0	3	180.0
20	H	12	1.0800	7	120.0	3	-60.0
21	H	12	1.0800	7	120.0	3	60.0
22	H	13	1.0800	7	120.0	3	180.0
23	H	13	1.0800	7	120.0	3	-60.0
24	H	13	1.0800	7	120.0	3	60.0
25	H	14	1.0800	8	120.0	4	180.0
26	H	14	1.0800	8	120.0	4	60.0
27	H	14	1.0800	8	120.0	4	-60.0
28	H	15	1.0800	8	120.0	4	180.0
29	H	15	1.0800	8	120.0	4	60.0
30	H	15	1.0800	8	120.0	4	-60.0

3A, ϕ = 120°:

1	C						
2	C	1	1.3525				
3	C	2	1.5646	1	120.0		
4	C	3	1.4936	2	120.0	1	180.0
5	C	4	1.5646	3	120.0	2	60.0
6	C	5	1.3525	4	120.0	3	180.0
7	C	3	1.4819	2	120.0	1	0.0
8	C	4	1.4819	5	120.0	6	0.0
9	H	1	1.0800	2	120.0	3	180.0
10	H	1	1.0800	2	120.0	3	0.0
11	H	2	1.0800	3	120.0	1	180.0
12	C	7	1.5400	3	120.0	2	0.0
13	C	7	1.5400	3	120.0	2	180.0
14	C	8	1.5400	4	120.0	5	0.0
15	C	8	1.5400	4	120.0	5	180.0
16	H	5	1.0800	4	120.0	6	180.0
17	H	6	1.0800	5	120.0	4	180.0
18	H	6	1.0800	5	120.0	4	0.0
19	H	12	1.0800	7	120.0	3	180.0
20	H	12	1.0800	7	120.0	3	-60.0
21	H	12	1.0800	7	120.0	3	60.0
22	H	13	1.0800	7	120.0	3	180.0
23	H	13	1.0800	7	120.0	3	-60.0
24	H	13	1.0800	7	120.0	3	60.0
25	H	14	1.0800	8	120.0	4	180.0
26	H	14	1.0800	8	120.0	4	60.0
27	H	14	1.0800	8	120.0	4	-60.0
28	H	15	1.0800	8	120.0	4	180.0
29	H	15	1.0800	8	120.0	4	60.0
30	H	15	1.0800	8	120.0	4	-60.0

3B, $\phi = 40°$:

1	C						
2	C	1	1.3384				
3	C	2	1.4876	1	120.0		
4	C	3	2.4077	2	120.0	1	0.0
5	C	4	1.4846	3	120.0	2	140.0
6	C	5	1.3384	4	120.0	3	0.0
7	C	3	1.3901	2	120.0	1	180.0
8	C	4	1.3901	5	120.0	6	180.0
9	H	1	1.0800	2	120.0	3	180.0
10	H	1	1.0800	2	120.0	3	0.0
11	H	2	1.0800	3	120.0	1	180.0
12	C	7	1.5400	3	120.0	2	0.0
13	C	7	1.5400	3	120.0	2	180.0
14	C	8	1.5400	4	120.0	5	0.0
15	C	8	1.5400	4	120.0	5	180.0
16	H	5	1.0800	4	120.0	6	180.0
17	H	6	1.0800	5	120.0	4	180.0
18	H	6	1.0800	5	120.0	4	0.0
19	H	12	1.0800	7	120.0	3	180.0
20	H	12	1.0800	7	120.0	3	-60.0
21	H	12	1.0800	7	120.0	3	60.0
22	H	13	1.0800	7	120.0	3	180.0
23	H	13	1.0800	7	120.0	3	-60.0
24	H	13	1.0800	7	120.0	3	60.0
25	H	14	1.0800	8	120.0	4	180.0
26	H	14	1.0800	8	120.0	4	60.0
27	H	14	1.0800	8	120.0	4	-60.0
28	H	15	1.0800	8	120.0	4	180.0
29	H	15	1.0800	8	120.0	4	60.0
30	H	15	1.0800	8	120.0	4	-60.0

3B, $\phi = 60°$:

1	C						
2	C	1	1.3574				
3	C	2	1.5039	1	120.0		
4	C	3	1.5264	2	120.0	1	0.0
5	C	4	1.5039	3	120.0	2	120.0
6	C	5	1.3574	4	120.0	3	0.0
7	C	3	1.3972	2	120.0	1	180.0
8	C	4	1.3972	5	120.0	6	180.0
9	H	1	1.0800	2	120.0	3	180.0
10	H	1	1.0800	2	120.0	3	0.0
11	H	2	1.0800	3	120.0	1	180.0
12	C	7	1.5400	3	120.0	2	0.0
13	C	7	1.5400	3	120.0	2	180.0
14	C	8	1.5400	4	120.0	5	0.0
15	C	8	1.5400	4	120.0	5	180.0
16	H	5	1.0800	4	120.0	6	180.0
17	H	6	1.0800	5	120.0	4	180.0
18	H	6	1.0800	5	120.0	4	0.0
19	H	12	1.0800	7	120.0	3	180.0
20	H	12	1.0800	7	120.0	3	-60.0
21	H	12	1.0800	7	120.0	3	60.0
22	H	13	1.0800	7	120.0	3	180.0
23	H	13	1.0800	7	120.0	3	-60.0
24	H	13	1.0800	7	120.0	3	60.0
25	H	14	1.0800	8	120.0	4	180.0
26	H	14	1.0800	8	120.0	4	60.0

27	H	14	1.0800	8	120.0	4	-60.0
28	H	15	1.0800	8	120.0	4	180.0
29	H	15	1.0800	8	120.0	4	60.0
30	H	15	1.0800	8	120.0	4	-60.0

3B, ϕ = 80°:

1	C						
2	C	1	1.3559				
3	C	2	1.4936	1	120.0		
4	C	3	1.5023	2	120.0	1	0.0
5	C	4	1.4936	3	120.0	2	100.0
6	C	5	1.3559	4	120.0	3	0.0
7	C	3	1.3851	2	120.0	1	180.0
8	C	4	1.3851	5	120.0	6	180.0
9	H	1	1.0800	2	120.0	3	180.0
10	H	1	1.0800	2	120.0	3	0.0
11	H	2	1.0800	3	120.0	1	180.0
12	C	7	1.5400	3	120.0	2	0.0
13	C	7	1.5400	3	120.0	2	180.0
14	C	8	1.5400	4	120.0	5	0.0
15	C	8	1.5400	4	120.0	5	180.0
16	H	5	1.0800	4	120.0	6	180.0
17	H	6	1.0800	5	120.0	4	180.0
18	H	6	1.0800	5	120.0	4	0.0
19	H	12	1.0800	7	120.0	3	180.0
20	H	12	1.0800	7	120.0	3	-60.0
21	H	12	1.0800	7	120.0	3	60.0
22	H	13	1.0800	7	120.0	3	180.0
23	H	13	1.0800	7	120.0	3	-60.0
24	H	13	1.0800	7	120.0	3	60.0
25	H	14	1.0800	8	120.0	4	180.0
26	H	14	1.0800	8	120.0	4	60.0
27	H	14	1.0800	8	120.0	4	-60.0
28	H	15	1.0800	8	120.0	4	180.0
29	H	15	1.0800	8	120.0	4	60.0
30	H	15	1.0800	8	120.0	4	-60.0

3B, ϕ = 100°:

1	C						
2	C	1	1.3556				
3	C	2	1.4923	1	120.0		
4	C	3	1.5029	2	120.0	1	0.0
5	C	4	1.4923	3	120.0	2	80.0
6	C	5	1.3556	4	120.0	3	0.0
7	C	3	1.3870	2	120.0	1	180.0
8	C	4	1.3870	5	120.0	6	180.0
9	H	1	1.0800	2	120.0	3	180.0
10	H	1	1.0800	2	120.0	3	0.0
11	H	2	1.0800	3	120.0	1	180.0
12	C	7	1.5400	3	120.0	2	0.0
13	C	7	1.5400	3	120.0	2	180.0
14	C	8	1.5400	4	120.0	5	0.0
15	C	8	1.5400	4	120.0	5	180.0
16	H	5	1.0800	4	120.0	6	180.0
17	H	6	1.0800	5	120.0	4	180.0
18	H	6	1.0800	5	120.0	4	0.0
19	H	12	1.0800	7	120.0	3	180.0
20	H	12	1.0800	7	120.0	3	-60.0
21	H	12	1.0800	7	120.0	3	60.0

22	H	13	1.0800	7	120.0	3	180.0
23	H	13	1.0800	7	120.0	3	-60.0
24	H	13	1.0800	7	120.0	3	60.0
25	H	14	1.0800	8	120.0	4	180.0
26	H	14	1.0800	8	120.0	4	60.0
27	H	14	1.0800	8	120.0	4	-60.0
28	H	15	1.0800	8	120.0	4	180.0
29	H	15	1.0800	8	120.0	4	60.0
30	H	15	1.0800	8	120.0	4	-60.0

3B, $\phi = 120°$:

1	C						
2	C	1	1.3575				
3	C	2	1.4953	1	120.0		
4	C	3	1.5396	2	120.0	1	0.0
5	C	4	1.4953	3	120.0	2	60.0
6	C	5	1.3575	4	120.0	3	0.0
7	C	3	1.4424	2	120.0	1	180.0
8	C	4	1.4424	5	120.0	6	180.0
9	H	1	1.0800	2	120.0	3	180.0
10	H	1	1.0800	2	120.0	3	0.0
11	H	2	1.0800	3	120.0	1	180.0
12	C	7	1.5400	3	120.0	2	0.0
13	C	7	1.5400	3	120.0	2	180.0
14	C	8	1.5400	4	120.0	5	0.0
15	C	8	1.5400	4	120.0	5	180.0
16	H	5	1.0800	4	120.0	6	180.0
17	H	6	1.0800	5	120.0	4	180.0
18	H	6	1.0800	5	120.0	4	0.0
19	H	12	1.0800	7	120.0	3	180.0
20	H	12	1.0800	7	120.0	3	-60.0
21	H	12	1.0800	7	120.0	3	60.0
22	H	13	1.0800	7	120.0	3	180.0
23	H	13	1.0800	7	120.0	3	-60.0
24	H	13	1.0800	7	120.0	3	60.0
25	H	14	1.0800	8	120.0	4	180.0
26	H	14	1.0800	8	120.0	4	60.0
27	H	14	1.0800	8	120.0	4	-60.0
28	H	15	1.0800	8	120.0	4	180.0
29	H	15	1.0800	8	120.0	4	60.0
30	H	15	1.0800	8	120.0	4	-60.0

3C, $\phi = 0°$:

```
 1     C
 2     C     1     1.3566
 3     C     2     1.4913     1     120.0
 4     C     3     1.4034     2     120.0     1     180.0
 5     C     4     1.4913     3     120.0     2     180.0
 6     C     5     1.3566     4     120.0     3     180.0
 7     C     3     1.4470     2     120.0     1       0.0
 8     C     4     1.4470     5     120.0     6       0.0
 9     H     1     1.0800     2     120.0     3     180.0
10     H     1     1.0800     2     120.0     3       0.0
11     H     2     1.0800     3     120.0     1     180.0
12     C     7     1.5400     3     120.0     2      90.0
13     C     7     1.5400     3     120.0     2     -90.0
14     C     8     1.5400     4     120.0     5      90.0
15     C     8     1.5400     4     120.0     5     -90.0
16     H     5     1.0800     4     120.0     6     180.0
17     H     6     1.0800     5     120.0     4     180.0
18     H     6     1.0800     5     120.0     4       0.0
19     H    12     1.0800     7     120.0     3     180.0
20     H    12     1.0800     7     120.0     3     -60.0
21     H    12     1.0800     7     120.0     3      60.0
22     H    13     1.0800     7     120.0     3     180.0
23     H    13     1.0800     7     120.0     3     -60.0
24     H    13     1.0800     7     120.0     3      60.0
25     H    14     1.0800     8     120.0     4     180.0
26     H    14     1.0800     8     120.0     4      60.0
27     H    14     1.0800     8     120.0     4     -60.0
28     H    15     1.0800     8     120.0     4     180.0
29     H    15     1.0800     8     120.0     4      60.0
30     H    15     1.0800     8     120.0     4     -60.0
```

3C, $\phi = 30°$:

```
 1     C
 2     C     1     1.3610
 3     C     2     1.4751     1     120.0
 4     C     3     1.4497     2     120.0     1     180.0
 5     C     4     1.4751     3     120.0     2     150.0
 6     C     5     1.3610     4     120.0     3     180.0
 7     C     3     1.4397     2     120.0     1       0.0
 8     C     4     1.4397     5     120.0     6       0.0
 9     H     1     1.0800     2     120.0     3     180.0
10     H     1     1.0800     2     120.0     3       0.0
11     H     2     1.0800     3     120.0     1     180.0
12     C     7     1.5400     3     120.0     2      90.0
13     C     7     1.5400     3     120.0     2     -90.0
14     C     8     1.5400     4     120.0     5      90.0
15     C     8     1.5400     4     120.0     5     -90.0
16     H     5     1.0800     4     120.0     6     180.0
17     H     6     1.0800     5     120.0     4     180.0
18     H     6     1.0800     5     120.0     4       0.0
19     H    12     1.0800     7     120.0     3     180.0
20     H    12     1.0800     7     120.0     3     -60.0
21     H    12     1.0800     7     120.0     3      60.0
22     H    13     1.0800     7     120.0     3     180.0
23     H    13     1.0800     7     120.0     3     -60.0
24     H    13     1.0800     7     120.0     3      60.0
25     H    14     1.0800     8     120.0     4     180.0
26     H    14     1.0800     8     120.0     4      60.0
```

```
27    H    14    1.0800    8    120.0    4    -60.0
28    H    15    1.0800    8    120.0    4    180.0
29    H    15    1.0800    8    120.0    4     60.0
30    H    15    1.0800    8    120.0    4    -60.0
```

3C, ϕ = 60°:

```
 1    C
 2    C     1    1.3640
 3    C     2    1.4635    1    120.0
 4    C     3    1.4745    2    120.0    1    180.0
 5    C     4    1.4635    3    120.0    2    120.0
 6    C     5    1.3640    4    120.0    3    180.0
 7    C     3    1.4376    2    120.0    1      0.0
 8    C     4    1.4376    5    120.0    6      0.0
 9    H     1    1.0800    2    120.0    3    180.0
10    H     1    1.0800    2    120.0    3      0.0
11    H     2    1.0800    3    120.0    1    180.0
12    C     7    1.5400    3    120.0    2     90.0
13    C     7    1.5400    3    120.0    2    -90.0
14    C     8    1.5400    4    120.0    5     90.0
15    C     8    1.5400    4    120.0    5    -90.0
16    H     5    1.0800    4    120.0    6    180.0
17    H     6    1.0800    5    120.0    4    180.0
18    H     6    1.0800    5    120.0    4      0.0
19    H    12    1.0800    7    120.0    3    180.0
20    H    12    1.0800    7    120.0    3    -60.0
21    H    12    1.0800    7    120.0    3     60.0
22    H    13    1.0800    7    120.0    3    180.0
23    H    13    1.0800    7    120.0    3    -60.0
24    H    13    1.0800    7    120.0    3     60.0
25    H    14    1.0800    8    120.0    4    180.0
26    H    14    1.0800    8    120.0    4     60.0
27    H    14    1.0800    8    120.0    4    -60.0
28    H    15    1.0800    8    120.0    4    180.0
29    H    15    1.0800    8    120.0    4     60.0
30    H    15    1.0800    8    120.0    4    -60.0
```

3C, ϕ = 90°:

```
 1    C
 2    C     1    1.3661
 3    C     2    1.4566    1    120.0
 4    C     3    1.4887    2    120.0    1    180.0
 5    C     4    1.4566    3    120.0    2     90.0
 6    C     5    1.3661    4    120.0    3    180.0
 7    C     3    1.4393    2    120.0    1      0.0
 8    C     4    1.4393    5    120.0    6      0.0
 9    H     1    1.0800    2    120.0    3    180.0
10    H     1    1.0800    2    120.0    3      0.0
11    H     2    1.0800    3    120.0    1    180.0
12    C     7    1.5400    3    120.0    2     90.0
13    C     7    1.5400    3    120.0    2    -90.0
14    C     8    1.5400    4    120.0    5     90.0
15    C     8    1.5400    4    120.0    5    -90.0
16    H     5    1.0800    4    120.0    6    180.0
17    H     6    1.0800    5    120.0    4    180.0
18    H     6    1.0800    5    120.0    4      0.0
19    H    12    1.0800    7    120.0    3    180.0
20    H    12    1.0800    7    120.0    3    -60.0
21    H    12    1.0800    7    120.0    3     60.0
```

22	H	13	1.0800	7	120.0	3	180.0
23	H	13	1.0800	7	120.0	3	-60.0
24	H	13	1.0800	7	120.0	3	60.0
25	H	14	1.0800	8	120.0	4	180.0
26	H	14	1.0800	8	120.0	4	60.0
27	H	14	1.0800	8	120.0	4	-60.0
28	H	15	1.0800	8	120.0	4	180.0
29	H	15	1.0800	8	120.0	4	60.0
30	H	15	1.0800	8	120.0	4	-60.0

3C, ϕ = 120°:

1	C						
2	C	1	1.3649				
3	C	2	1.4614	1	120.0		
4	C	3	1.4673	2	120.0	1	180.0
5	C	4	1.4614	3	120.0	2	60.0
6	C	5	1.3649	4	120.0	3	180.0
7	C	3	1.4448	2	120.0	1	0.0
8	C	4	1.4448	5	120.0	6	0.0
9	H	1	1.0800	2	120.0	3	180.0
10	H	1	1.0800	2	120.0	3	0.0
11	H	2	1.0800	3	120.0	1	180.0
12	C	7	1.5400	3	120.0	2	90.0
13	C	7	1.5400	3	120.0	2	-90.0
14	C	8	1.5400	4	120.0	5	90.0
15	C	8	1.5400	4	120.0	5	-90.0
16	H	5	1.0800	4	120.0	6	180.0
17	H	6	1.0800	5	120.0	4	180.0
18	H	6	1.0800	5	120.0	4	0.0
19	H	12	1.0800	7	120.0	3	180.0
20	H	12	1.0800	7	120.0	3	-60.0
21	H	12	1.0800	7	120.0	3	60.0
22	H	13	1.0800	7	120.0	3	180.0
23	H	13	1.0800	7	120.0	3	-60.0
24	H	13	1.0800	7	120.0	3	60.0
25	H	14	1.0800	8	120.0	4	180.0
26	H	14	1.0800	8	120.0	4	60.0
27	H	14	1.0800	8	120.0	4	-60.0
28	H	15	1.0800	8	120.0	4	180.0
29	H	15	1.0800	8	120.0	4	60.0
30	H	15	1.0800	8	120.0	4	-60.0

3D, $\phi = 0°$:

1	C						
2	C	1	1.3477				
3	C	2	1.5295	1	120.0		
4	C	3	1.5042	2	120.0	1	0.0
5	C	4	1.5295	3	120.0	2	180.0
6	C	5	1.3477	4	120.0	3	0.0
7	C	3	1.4313	2	120.0	1	180.0
8	C	4	1.4313	5	120.0	6	180.0
9	H	1	1.0800	2	120.0	3	180.0
10	H	1	1.0800	2	120.0	3	0.0
11	H	2	1.0800	3	120.0	1	180.0
12	C	7	1.5400	3	120.0	2	90.0
13	C	7	1.5400	3	120.0	2	-90.0
14	C	8	1.5400	4	120.0	5	90.0
15	C	8	1.5400	4	120.0	5	-90.0
16	H	5	1.0800	4	120.0	6	180.0
17	H	6	1.0800	5	120.0	4	180.0
18	H	6	1.0800	5	120.0	4	0.0
19	H	12	1.0800	7	120.0	3	180.0
20	H	12	1.0800	7	120.0	3	-60.0
21	H	12	1.0800	7	120.0	3	60.0
22	H	13	1.0800	7	120.0	3	180.0
23	H	13	1.0800	7	120.0	3	-60.0
24	H	13	1.0800	7	120.0	3	60.0
25	H	14	1.0800	8	120.0	4	180.0
26	H	14	1.0800	8	120.0	4	60.0
27	H	14	1.0800	8	120.0	4	-60.0
28	H	15	1.0800	8	120.0	4	180.0
29	H	15	1.0800	8	120.0	4	60.0
30	H	15	1.0800	8	120.0	4	-60.0

3D, $\phi = 30°$:

1	C						
2	C	1	1.3360				
3	C	2	1.4844	1	120.0		
4	C	3	1.8841	2	120.0	1	0.0
5	C	4	1.4844	3	120.0	2	150.0
6	C	5	1.3360	4	120.0	3	0.0
7	C	3	1.4152	2	120.0	1	180.0
8	C	4	1.4152	5	120.0	6	180.0
9	H	1	1.0800	2	120.0	3	180.0
10	H	1	1.0800	2	120.0	3	0.0
11	H	2	1.0800	3	120.0	1	180.0
12	C	7	1.5400	3	120.0	2	90.0
13	C	7	1.5400	3	120.0	2	-90.0
14	C	8	1.5400	4	120.0	5	90.0
15	C	8	1.5400	4	120.0	5	-90.0
16	H	5	1.0800	4	120.0	6	180.0
17	H	6	1.0800	5	120.0	4	180.0
18	H	6	1.0800	5	120.0	4	0.0
19	H	12	1.0800	7	120.0	3	180.0
20	H	12	1.0800	7	120.0	3	-60.0
21	H	12	1.0800	7	120.0	3	60.0
22	H	13	1.0800	7	120.0	3	180.0
23	H	13	1.0800	7	120.0	3	-60.0
24	H	13	1.0800	7	120.0	3	60.0
25	H	14	1.0800	8	120.0	4	180.0
26	H	14	1.0800	8	120.0	4	60.0

```
27    H    14    1.0800    8    120.0    4    -60.0
28    H    15    1.0800    8    120.0    4    180.0
29    H    15    1.0800    8    120.0    4     60.0
30    H    15    1.0800    8    120.0    4    -60.0
```

3D, ϕ = 90°:

```
 1    C
 2    C     1    1.3610
 3    C     2    1.4724    1    120.0
 4    C     3    1.5064    2    120.0    1      0.0
 5    C     4    1.4724    3    120.0    2     90.0
 6    C     5    1.3610    4    120.0    3      0.0
 7    C     3    1.4318    2    120.0    1    180.0
 8    C     4    1.4318    5    120.0    6    180.0
 9    H     1    1.0800    2    120.0    3    180.0
10    H     1    1.0800    2    120.0    3      0.0
11    H     2    1.0800    3    120.0    1    180.0
12    C     7    1.5400    3    120.0    2     90.0
13    C     7    1.5400    3    120.0    2    -90.0
14    C     8    1.5400    4    120.0    5     90.0
15    C     8    1.5400    4    120.0    5    -90.0
16    H     5    1.0800    4    120.0    6    180.0
17    H     6    1.0800    5    120.0    4    180.0
18    H     6    1.0800    5    120.0    4      0.0
19    H    12    1.0800    7    120.0    3    180.0
20    H    12    1.0800    7    120.0    3    -60.0
21    H    12    1.0800    7    120.0    3     60.0
22    H    13    1.0800    7    120.0    3    180.0
23    H    13    1.0800    7    120.0    3    -60.0
24    H    13    1.0800    7    120.0    3     60.0
25    H    14    1.0800    8    120.0    4    180.0
26    H    14    1.0800    8    120.0    4     60.0
27    H    14    1.0800    8    120.0    4    -60.0
28    H    15    1.0800    8    120.0    4    180.0
29    H    15    1.0800    8    120.0    4     60.0
30    H    15    1.0800    8    120.0    4    -60.0
```

3D, ϕ = 120°:

```
 1    C
 2    C     1    1.3630
 3    C     2    1.4839    1    120.0
 4    C     3    1.4936    2    120.0    1      0.0
 5    C     4    1.4839    3    120.0    2     60.0
 6    C     5    1.3630    4    120.0    3      0.0
 7    C     3    1.4309    2    120.0    1    180.0
 8    C     4    1.4309    5    120.0    6    180.0
 9    H     1    1.0800    2    120.0    3    180.0
10    H     1    1.0800    2    120.0    3      0.0
11    H     2    1.0800    3    120.0    1    180.0
12    C     7    1.5400    3    120.0    2     90.0
13    C     7    1.5400    3    120.0    2    -90.0
14    C     8    1.5400    4    120.0    5     90.0
15    C     8    1.5400    4    120.0    5    -90.0
16    H     5    1.0800    4    120.0    6    180.0
17    H     6    1.0800    5    120.0    4    180.0
18    H     6    1.0800    5    120.0    4      0.0
19    H    12    1.0800    7    120.0    3    180.0
20    H    12    1.0800    7    120.0    3    -60.0
21    H    12    1.0800    7    120.0    3     60.0
```

22	H	13	1.0800	7	120.0	3	180.0
23	H	13	1.0800	7	120.0	3	-60.0
24	H	13	1.0800	7	120.0	3	60.0
25	H	14	1.0800	8	120.0	4	180.0
26	H	14	1.0800	8	120.0	4	60.0
27	H	14	1.0800	8	120.0	4	-60.0
28	H	15	1.0800	8	120.0	4	180.0
29	H	15	1.0800	8	120.0	4	60.0
30	H	15	1.0800	8	120.0	4	-60.0

5A, ϕ = 0°:

1	C						
2	C	1	1.4290				
3	C	2	1.5084	1	120.0		
4	C	3	1.6412	2	120.0	1	180.0
5	C	4	1.5084	3	120.0	2	180.0
6	C	5	1.4290	4	120.0	3	180.0
7	C	3	1.5262	2	120.0	1	0.0
8	C	4	1.5262	5	120.0	6	0.0
9	H	1	1.0800	2	120.0	3	0.0
10	H	2	1.0800	3	120.0	1	180.0
11	C	7	1.5400	3	120.0	2	180.0
12	C	7	1.5400	3	120.0	2	0.0
13	C	8	1.5400	4	120.0	5	180.0
14	C	8	1.5400	4	120.0	5	0.0
15	H	5	1.0800	4	120.0	6	180.0
16	H	6	1.0800	5	120.0	4	0.0
17	C	1	1.3871	2	120.0	3	180.0
18	C	6	1.3871	5	120.0	4	180.0
19	H	17	1.0800	1	120.0	2	180.0
20	H	17	1.0800	1	120.0	2	0.0
21	H	18	1.0800	6	120.0	5	180.0
22	H	18	1.0800	6	120.0	5	0.0
23	H	11	1.0800	7	120.0	3	180.0
24	H	11	1.0800	7	120.0	3	-60.0
25	H	11	1.0800	7	120.0	3	60.0
26	H	12	1.0800	7	120.0	3	180.0
27	H	12	1.0800	7	120.0	3	-60.0
28	H	12	1.0800	7	120.0	3	60.0
29	H	13	1.0800	8	120.0	4	180.0
30	H	13	1.0800	8	120.0	4	60.0
31	H	13	1.0800	8	120.0	4	-60.0
32	H	14	1.0800	8	120.0	4	180.0
33	H	14	1.0800	8	120.0	4	60.0
34	H	14	1.0800	8	120.0	4	-60.0

5A, ϕ = 20°:

1	C						
2	C	1	1.4287				
3	C	2	1.5082	1	120.0		
4	C	3	1.6089	2	120.0	1	180.0
5	C	4	1.5082	3	120.0	2	160.0
6	C	5	1.4287	4	120.0	3	180.0
7	C	3	1.5267	2	120.0	1	0.0
8	C	4	1.5267	5	120.0	6	0.0
9	H	1	1.0800	2	120.0	3	0.0
10	H	2	1.0800	3	120.0	1	180.0
11	C	7	1.5400	3	120.0	2	180.0
12	C	7	1.5400	3	120.0	2	0.0
13	C	8	1.5400	4	120.0	5	180.0
14	C	8	1.5400	4	120.0	5	0.0
15	H	5	1.0800	4	120.0	6	180.0
16	H	6	1.0800	5	120.0	4	0.0
17	C	1	1.3875	2	120.0	3	180.0
18	C	6	1.3875	5	120.0	4	180.0
19	H	17	1.0800	1	120.0	2	180.0
20	H	17	1.0800	1	120.0	2	0.0
21	H	18	1.0800	6	120.0	5	180.0
22	H	18	1.0800	6	120.0	5	0.0

23	H	11	1.0800	7	120.0	3	180.0
24	H	11	1.0800	7	120.0	3	-60.0
25	H	11	1.0800	7	120.0	3	60.0
26	H	12	1.0800	7	120.0	3	180.0
27	H	12	1.0800	7	120.0	3	-60.0
28	H	12	1.0800	7	120.0	3	60.0
29	H	13	1.0800	8	120.0	4	180.0
30	H	13	1.0800	8	120.0	4	60.0
31	H	13	1.0800	8	120.0	4	-60.0
32	H	14	1.0800	8	120.0	4	180.0
33	H	14	1.0800	8	120.0	4	60.0
34	H	14	1.0800	8	120.0	4	-60.0

5A, ϕ = 40°:

1	C						
2	C	1	1.4268				
3	C	2	1.5225	1	120.0		
4	C	3	1.5201	2	120.0	1	180.0
5	C	4	1.5225	3	120.0	2	140.0
6	C	5	1.4268	4	120.0	3	180.0
7	C	3	1.5015	2	120.0	1	0.0
8	C	4	1.5015	5	120.0	6	0.0
9	H	1	1.0800	2	120.0	3	0.0
10	H	2	1.0800	3	120.0	1	180.0
11	C	7	1.5400	3	120.0	2	180.0
12	C	7	1.5400	3	120.0	2	0.0
13	C	8	1.5400	4	120.0	5	180.0
14	C	8	1.5400	4	120.0	5	0.0
15	H	5	1.0800	4	120.0	6	180.0
16	H	6	1.0800	5	120.0	4	0.0
17	C	1	1.3892	2	120.0	3	180.0
18	C	6	1.3892	5	120.0	4	180.0
19	H	17	1.0800	1	120.0	2	180.0
20	H	17	1.0800	1	120.0	2	0.0
21	H	18	1.0800	6	120.0	5	180.0
22	H	18	1.0800	6	120.0	5	0.0
23	H	11	1.0800	7	120.0	3	180.0
24	H	11	1.0800	7	120.0	3	-60.0
25	H	11	1.0800	7	120.0	3	60.0
26	H	12	1.0800	7	120.0	3	180.0
27	H	12	1.0800	7	120.0	3	-60.0
28	H	12	1.0800	7	120.0	3	60.0
29	H	13	1.0800	8	120.0	4	180.0
30	H	13	1.0800	8	120.0	4	60.0
31	H	13	1.0800	8	120.0	4	-60.0
32	H	14	1.0800	8	120.0	4	180.0
33	H	14	1.0800	8	120.0	4	60.0
34	H	14	1.0800	8	120.0	4	-60.0

5A, ϕ = 60°:

1	C						
2	C	1	1.4259				
3	C	2	1.5304	1	120.0		
4	C	3	1.4820	2	120.0	1	180.0
5	C	4	1.5304	3	120.0	2	120.0
6	C	5	1.4259	4	120.0	3	180.0
7	C	3	1.4804	2	120.0	1	0.0
8	C	4	1.5262	5	120.0	6	0.0
9	H	1	1.0800	2	120.0	3	0.0

10	H	2	1.0800	3	120.0	1	180.0
11	C	7	1.5400	3	120.0	2	180.0
12	C	7	1.5400	3	120.0	2	0.0
13	C	8	1.5400	4	120.0	5	180.0
14	C	8	1.5400	4	120.0	5	0.0
15	H	5	1.0800	4	120.0	6	180.0
16	H	6	1.0800	5	120.0	4	0.0
17	C	1	1.3899	2	120.0	3	180.0
18	C	6	1.3899	5	120.0	4	180.0
19	H	17	1.0800	1	120.0	2	180.0
20	H	17	1.0800	1	120.0	2	0.0
21	H	18	1.0800	6	120.0	5	180.0
22	H	18	1.0800	6	120.0	5	0.0
23	H	11	1.0800	7	120.0	3	180.0
24	H	11	1.0800	7	120.0	3	-60.0
25	H	11	1.0800	7	120.0	3	60.0
26	H	12	1.0800	7	120.0	3	180.0
27	H	12	1.0800	7	120.0	3	-60.0
28	H	12	1.0800	7	120.0	3	60.0
29	H	13	1.0800	8	120.0	4	180.0
30	H	13	1.0800	8	120.0	4	60.0
31	H	13	1.0800	8	120.0	4	-60.0
32	H	14	1.0800	8	120.0	4	180.0
33	H	14	1.0800	8	120.0	4	60.0
34	H	14	1.0800	8	120.0	4	-60.0

5A, ϕ = 80°:

1	C						
2	C	1	1.4262				
3	C	2	1.5295	1	120.0		
4	C	3	1.4743	2	120.0	1	180.0
5	C	4	1.5295	3	120.0	2	100.0
6	C	5	1.4262	4	120.0	3	180.0
7	C	3	1.4766	2	120.0	1	0.0
8	C	4	1.4755	5	120.0	6	0.0
9	H	1	1.0800	2	120.0	3	0.0
10	H	2	1.0800	3	120.0	1	180.0
11	C	7	1.5400	3	120.0	2	180.0
12	C	7	1.5400	3	120.0	2	0.0
13	C	8	1.5400	4	120.0	5	180.0
14	C	8	1.5400	4	120.0	5	0.0
15	H	5	1.0800	4	120.0	6	180.0
16	H	6	1.0800	5	120.0	4	0.0
17	C	1	1.3896	2	120.0	3	180.0
18	C	6	1.3896	5	120.0	4	180.0
19	H	17	1.0800	1	120.0	2	180.0
20	H	17	1.0800	1	120.0	2	0.0
21	H	18	1.0800	6	120.0	5	180.0
22	H	18	1.0800	6	120.0	5	0.0
23	H	11	1.0800	7	120.0	3	180.0
24	H	11	1.0800	7	120.0	3	-60.0
25	H	11	1.0800	7	120.0	3	60.0
26	H	12	1.0800	7	120.0	3	180.0
27	H	12	1.0800	7	120.0	3	-60.0
28	H	12	1.0800	7	120.0	3	60.0
29	H	13	1.0800	8	120.0	4	180.0
30	H	13	1.0800	8	120.0	4	60.0
31	H	13	1.0800	8	120.0	4	-60.0
32	H	14	1.0800	8	120.0	4	180.0

33	H	14	1.0800	8	120.0	4	60.0
34	H	14	1.0800	8	120.0	4	-60.0

5A, $\phi = 100°$:

1	C						
2	C	1	1.4269				
3	C	2	1.5257	1	120.0		
4	C	3	1.4749	2	120.0	1	180.0
5	C	4	1.5257	3	120.0	2	80.0
6	C	5	1.4269	4	120.0	3	180.0
7	C	3	1.4822	2	120.0	1	0.0
8	C	4	1.4822	5	120.0	6	0.0
9	H	1	1.0800	2	120.0	3	0.0
10	H	2	1.0800	3	120.0	1	180.0
11	C	7	1.5400	3	120.0	2	180.0
12	C	7	1.5400	3	120.0	2	0.0
13	C	8	1.5400	4	120.0	5	180.0
14	C	8	1.5400	4	120.0	5	0.0
15	H	5	1.0800	4	120.0	6	180.0
16	H	6	1.0800	5	120.0	4	0.0
17	C	1	1.3900	2	120.0	3	180.0
18	C	6	1.3900	5	120.0	4	180.0
19	H	17	1.0800	1	120.0	2	180.0
20	H	17	1.0800	1	120.0	2	0.0
21	H	18	1.0800	6	120.0	5	180.0
22	H	18	1.0800	6	120.0	5	0.0
23	H	11	1.0800	7	120.0	3	180.0
24	H	11	1.0800	7	120.0	3	-60.0
25	H	11	1.0800	7	120.0	3	60.0
26	H	12	1.0800	7	120.0	3	180.0
27	H	12	1.0800	7	120.0	3	-60.0
28	H	12	1.0800	7	120.0	3	60.0
29	H	13	1.0800	8	120.0	4	180.0
30	H	13	1.0800	8	120.0	4	60.0
31	H	13	1.0800	8	120.0	4	-60.0
32	H	14	1.0800	8	120.0	4	180.0
33	H	14	1.0800	8	120.0	4	60.0
34	H	14	1.0800	8	120.0	4	-60.0

5A, $\phi = 120°$:

1	C						
2	C	1	1.4292				
3	C	2	1.5054	1	120.0		
4	C	3	1.4956	2	120.0	1	180.0
5	C	4	1.5054	3	120.0	2	60.0
6	C	5	1.4292	4	120.0	3	180.0
7	C	3	1.5298	2	120.0	1	0.0
8	C	4	1.5298	5	120.0	6	0.0
9	H	1	1.0800	2	120.0	3	0.0
10	H	2	1.0800	3	120.0	1	180.0
11	C	7	1.5400	3	120.0	2	180.0
12	C	7	1.5400	3	120.0	2	0.0
13	C	8	1.5400	4	120.0	5	180.0
14	C	8	1.5400	4	120.0	5	0.0
15	H	5	1.0800	4	120.0	6	180.0
16	H	6	1.0800	5	120.0	4	0.0
17	C	1	1.3865	2	120.0	3	180.0
18	C	6	1.3865	5	120.0	4	180.0
19	H	17	1.0800	1	120.0	2	180.0

20	H	17	1.0800	1	120.0	2	0.0
21	H	18	1.0800	6	120.0	5	180.0
22	H	18	1.0800	6	120.0	5	0.0
23	H	11	1.0800	7	120.0	3	180.0
24	H	11	1.0800	7	120.0	3	-60.0
25	H	11	1.0800	7	120.0	3	60.0
26	H	12	1.0800	7	120.0	3	180.0
27	H	12	1.0800	7	120.0	3	-60.0
28	H	12	1.0800	7	120.0	3	60.0
29	H	13	1.0800	8	120.0	4	180.0
30	H	13	1.0800	8	120.0	4	60.0
31	H	13	1.0800	8	120.0	4	-60.0
32	H	14	1.0800	8	120.0	4	180.0
33	H	14	1.0800	8	120.0	4	60.0
34	H	14	1.0800	8	120.0	4	-60.0

5B, ϕ = 40°:

1	C						
2	C	1	1.4202				
3	C	2	1.4215	1	120.0		
4	C	3	2.8518	2	120.0	1	0.0
5	C	4	1.4215	3	120.0	2	140.0
6	C	5	1.4202	4	120.0	3	0.0
7	C	3	1.3984	2	120.0	1	180.0
8	C	4	1.3984	5	120.0	6	180.0
9	H	1	1.0800	2	120.0	3	0.0
10	H	2	1.0800	3	120.0	1	180.0
11	C	7	1.5400	3	120.0	2	180.0
12	C	7	1.5400	3	120.0	2	0.0
13	C	8	1.5400	4	120.0	5	180.0
14	C	8	1.5400	4	120.0	5	0.0
15	H	5	1.0800	4	120.0	6	180.0
16	H	6	1.0800	5	120.0	4	0.0
17	C	1	1.3858	2	120.0	3	180.0
18	C	6	1.3858	5	120.0	4	180.0
19	H	17	1.0800	1	120.0	2	180.0
20	H	17	1.0800	1	120.0	2	0.0
21	H	18	1.0800	6	120.0	5	180.0
22	H	18	1.0800	6	120.0	5	0.0
23	H	11	1.0800	7	120.0	3	180.0
24	H	11	1.0800	7	120.0	3	-60.0
25	H	11	1.0800	7	120.0	3	60.0
26	H	12	1.0800	7	120.0	3	180.0
27	H	12	1.0800	7	120.0	3	-60.0
28	H	12	1.0800	7	120.0	3	60.0
29	H	13	1.0800	8	120.0	4	180.0
30	H	13	1.0800	8	120.0	4	60.0
31	H	13	1.0800	8	120.0	4	-60.0
32	H	14	1.0800	8	120.0	4	180.0
33	H	14	1.0800	8	120.0	4	60.0
34	H	14	1.0800	8	120.0	4	-60.0

5B, ϕ = 60°:

1	C						
2	C	1	1.4359				
3	C	2	1.4556	1	120.0		
4	C	3	1.5292	2	120.0	1	0.0
5	C	4	1.4556	3	120.0	2	120.0
6	C	5	1.4359	4	120.0	3	0.0
7	C	3	1.4357	2	120.0	1	180.0
8	C	4	1.4357	5	120.0	6	180.0
9	H	1	1.0800	2	120.0	3	0.0
10	H	2	1.0800	3	120.0	1	180.0
11	C	7	1.5400	3	120.0	2	180.0
12	C	7	1.5400	3	120.0	2	0.0
13	C	8	1.5400	4	120.0	5	180.0
14	C	8	1.5400	4	120.0	5	0.0
15	H	5	1.0800	4	120.0	6	180.0
16	H	6	1.0800	5	120.0	4	0.0
17	C	1	1.3862	2	120.0	3	180.0
18	C	6	1.3862	5	120.0	4	180.0
19	H	17	1.0800	1	120.0	2	180.0
20	H	17	1.0800	1	120.0	2	0.0
21	H	18	1.0800	6	120.0	5	180.0
22	H	18	1.0800	6	120.0	5	0.0

23	H	11	1.0800	7	120.0	3	180.0
24	H	11	1.0800	7	120.0	3	-60.0
25	H	11	1.0800	7	120.0	3	60.0
26	H	12	1.0800	7	120.0	3	180.0
27	H	12	1.0800	7	120.0	3	-60.0
28	H	12	1.0800	7	120.0	3	60.0
29	H	13	1.0800	8	120.0	4	180.0
30	H	13	1.0800	8	120.0	4	60.0
31	H	13	1.0800	8	120.0	4	-60.0
32	H	14	1.0800	8	120.0	4	180.0
33	H	14	1.0800	8	120.0	4	60.0
34	H	14	1.0800	8	120.0	4	-60.0

5B, ϕ = 80°:

1	C						
2	C	1	1.4332				
3	C	2	1.4470	1	120.0		
4	C	3	1.5052	2	120.0	1	0.0
5	C	4	1.4470	3	120.0	2	100.0
6	C	5	1.4332	4	120.0	3	0.0
7	C	3	1.4226	2	120.0	1	180.0
8	C	4	1.4226	5	120.0	6	180.0
9	H	1	1.0800	2	120.0	3	0.0
10	H	2	1.0800	3	120.0	1	180.0
11	C	7	1.5400	3	120.0	2	180.0
12	C	7	1.5400	3	120.0	2	0.0
13	C	8	1.5400	4	120.0	5	180.0
14	C	8	1.5400	4	120.0	5	0.0
15	H	5	1.0800	4	120.0	6	180.0
16	H	6	1.0800	5	120.0	4	0.0
17	C	1	1.3853	2	120.0	3	180.0
18	C	6	1.3853	5	120.0	4	180.0
19	H	17	1.0800	1	120.0	2	180.0
20	H	17	1.0800	1	120.0	2	0.0
21	H	18	1.0800	6	120.0	5	180.0
22	H	18	1.0800	6	120.0	5	0.0
23	H	11	1.0800	7	120.0	3	180.0
24	H	11	1.0800	7	120.0	3	-60.0
25	H	11	1.0800	7	120.0	3	60.0
26	H	12	1.0800	7	120.0	3	180.0
27	H	12	1.0800	7	120.0	3	-60.0
28	H	12	1.0800	7	120.0	3	60.0
29	H	13	1.0800	8	120.0	4	180.0
30	H	13	1.0800	8	120.0	4	60.0
31	H	13	1.0800	8	120.0	4	-60.0
32	H	14	1.0800	8	120.0	4	180.0
33	H	14	1.0800	8	120.0	4	60.0
34	H	14	1.0800	8	120.0	4	-60.0

5B, ϕ = 100°:

1	C						
2	C	1	1.4340				
3	C	2	1.4448	1	120.0		
4	C	3	1.5055	2	120.0	1	0.0
5	C	4	1.4448	3	120.0	2	80.0
6	C	5	1.4340	4	120.0	3	0.0
7	C	3	1.4258	2	120.0	1	180.0
8	C	4	1.4258	5	120.0	6	180.0
9	H	1	1.0800	2	120.0	3	0.0

10	H	2	1.0800	3	120.0	1	180.0
11	C	7	1.5400	3	120.0	2	180.0
12	C	7	1.5400	3	120.0	2	0.0
13	C	8	1.5400	4	120.0	5	180.0
14	C	8	1.5400	4	120.0	5	0.0
15	H	5	1.0800	4	120.0	6	180.0
16	H	6	1.0800	5	120.0	4	0.0
17	C	1	1.3844	2	120.0	3	180.0
18	C	6	1.3844	5	120.0	4	180.0
19	H	17	1.0800	1	120.0	2	180.0
20	H	17	1.0800	1	120.0	2	0.0
21	H	18	1.0800	6	120.0	5	180.0
22	H	18	1.0800	6	120.0	5	0.0
23	H	11	1.0800	7	120.0	3	180.0
24	H	11	1.0800	7	120.0	3	-60.0
25	H	11	1.0800	7	120.0	3	60.0
26	H	12	1.0800	7	120.0	3	180.0
27	H	12	1.0800	7	120.0	3	-60.0
28	H	12	1.0800	7	120.0	3	60.0
29	H	13	1.0800	8	120.0	4	180.0
30	H	13	1.0800	8	120.0	4	60.0
31	H	13	1.0800	8	120.0	4	-60.0
32	H	14	1.0800	8	120.0	4	180.0
33	H	14	1.0800	8	120.0	4	60.0
34	H	14	1.0800	8	120.0	4	-60.0

5B, $\phi = 120°$:

1	C						
2	C	1	1.4402				
3	C	2	1.4424	1	120.0		
4	C	3	1.5417	2	120.0	1	0.0
5	C	4	1.4424	3	120.0	2	60.0
6	C	5	1.4402	4	120.0	3	0.0
7	C	3	1.4649	2	120.0	1	180.0
8	C	4	1.4649	5	120.0	6	180.0
9	H	1	1.0800	2	120.0	3	0.0
10	H	2	1.0800	3	120.0	1	180.0
11	C	7	1.5400	3	120.0	2	180.0
12	C	7	1.5400	3	120.0	2	0.0
13	C	8	1.5400	4	120.0	5	180.0
14	C	8	1.5400	4	120.0	5	0.0
15	H	5	1.0800	4	120.0	6	180.0
16	H	6	1.0800	5	120.0	4	0.0
17	C	1	1.3818	2	120.0	3	180.0
18	C	6	1.3818	5	120.0	4	180.0
19	H	17	1.0800	1	120.0	2	180.0
20	H	17	1.0800	1	120.0	2	0.0
21	H	18	1.0800	6	120.0	5	180.0
22	H	18	1.0800	6	120.0	5	0.0
23	H	11	1.0800	7	120.0	3	180.0
24	H	11	1.0800	7	120.0	3	-60.0
25	H	11	1.0800	7	120.0	3	60.0
26	H	12	1.0800	7	120.0	3	180.0
27	H	12	1.0800	7	120.0	3	-60.0
28	H	12	1.0800	7	120.0	3	60.0
29	H	13	1.0800	8	120.0	4	180.0
30	H	13	1.0800	8	120.0	4	60.0
31	H	13	1.0800	8	120.0	4	-60.0
32	H	14	1.0800	8	120.0	4	180.0

33	H	14	1.0800	8	120.0	4	60.0
34	H	14	1.0800	8	120.0	4	-60.0

5C, ϕ = 0°:

1	C						
2	C	1	1.4616				
3	C	2	1.3904	1	120.0		
4	C	3	1.4977	2	120.0	1	180.0
5	C	4	1.3904	3	120.0	2	180.0
6	C	5	1.4616	4	120.0	3	180.0
7	C	3	1.4819	2	120.0	1	0.0
8	C	4	1.4819	5	120.0	6	0.0
9	H	1	1.0800	2	120.0	3	0.0
10	H	2	1.0800	3	120.0	1	180.0
11	C	7	1.5400	3	120.0	2	90.0
12	C	7	1.5400	3	120.0	2	-90.0
13	C	8	1.5400	4	120.0	5	90.0
14	C	8	1.5400	4	120.0	5	-90.0
15	H	5	1.0800	4	120.0	6	180.0
16	H	6	1.0800	5	120.0	4	0.0
17	C	1	1.3655	2	120.0	3	180.0
18	C	6	1.3655	5	120.0	4	180.0
19	H	17	1.0800	1	120.0	2	180.0
20	H	17	1.0800	1	120.0	2	0.0
21	H	18	1.0800	6	120.0	5	180.0
22	H	18	1.0800	6	120.0	5	0.0
23	H	11	1.0800	7	120.0	3	180.0
24	H	11	1.0800	7	120.0	3	-60.0
25	H	11	1.0800	7	120.0	3	60.0
26	H	12	1.0800	7	120.0	3	180.0
27	H	12	1.0800	7	120.0	3	-60.0
28	H	12	1.0800	7	120.0	3	60.0
29	H	13	1.0800	8	120.0	4	180.0
30	H	13	1.0800	8	120.0	4	60.0
31	H	13	1.0800	8	120.0	4	-60.0
32	H	14	1.0800	8	120.0	4	180.0
33	H	14	1.0800	8	120.0	4	60.0
34	H	14	1.0800	8	120.0	4	-60.0

5C, ϕ = 20°:

1	C						
2	C	1	1.4618				
3	C	2	1.3900	1	120.0		
4	C	3	1.5000	2	120.0	1	180.0
5	C	4	1.3900	3	120.0	2	160.0
6	C	5	1.4618	4	120.0	3	180.0
7	C	3	1.4824	2	120.0	1	0.0
8	C	4	1.4824	5	120.0	6	0.0
9	H	1	1.0800	2	120.0	3	0.0
10	H	2	1.0800	3	120.0	1	180.0
11	C	7	1.5400	3	120.0	2	90.0
12	C	7	1.5400	3	120.0	2	-90.0
13	C	8	1.5400	4	120.0	5	90.0
14	C	8	1.5400	4	120.0	5	-90.0
15	H	5	1.0800	4	120.0	6	180.0
16	H	6	1.0800	5	120.0	4	0.0
17	C	1	1.3656	2	120.0	3	180.0
18	C	6	1.3656	5	120.0	4	180.0
19	H	17	1.0800	1	120.0	2	180.0
20	H	17	1.0800	1	120.0	2	0.0
21	H	18	1.0800	6	120.0	5	180.0
22	H	18	1.0800	6	120.0	5	0.0

23	H	11	1.0800	7	120.0	3	180.0
24	H	11	1.0800	7	120.0	3	-60.0
25	H	11	1.0800	7	120.0	3	60.0
26	H	12	1.0800	7	120.0	3	180.0
27	H	12	1.0800	7	120.0	3	-60.0
28	H	12	1.0800	7	120.0	3	60.0
29	H	13	1.0800	8	120.0	4	180.0
30	H	13	1.0800	8	120.0	4	60.0
31	H	13	1.0800	8	120.0	4	-60.0
32	H	14	1.0800	8	120.0	4	180.0
33	H	14	1.0800	8	120.0	4	60.0
34	H	14	1.0800	8	120.0	4	-60.0

5C, ϕ = 40°:

1	C						
2	C	1	1.4620				
3	C	2	1.3888	1	120.0		
4	C	3	1.5010	2	120.0	1	180.0
5	C	4	1.3888	3	120.0	2	140.0
6	C	5	1.4620	4	120.0	3	180.0
7	C	3	1.4837	2	120.0	1	0.0
8	C	4	1.4837	5	120.0	6	0.0
9	H	1	1.0800	2	120.0	3	0.0
10	H	2	1.0800	3	120.0	1	180.0
11	C	7	1.5400	3	120.0	2	90.0
12	C	7	1.5400	3	120.0	2	-90.0
13	C	8	1.5400	4	120.0	5	90.0
14	C	8	1.5400	4	120.0	5	-90.0
15	H	5	1.0800	4	120.0	6	180.0
16	H	6	1.0800	5	120.0	4	0.0
17	C	1	1.3657	2	120.0	3	180.0
18	C	6	1.3657	5	120.0	4	180.0
19	H	17	1.0800	1	120.0	2	180.0
20	H	17	1.0800	1	120.0	2	0.0
21	H	18	1.0800	6	120.0	5	180.0
22	H	18	1.0800	6	120.0	5	0.0
23	H	11	1.0800	7	120.0	3	180.0
24	H	11	1.0800	7	120.0	3	-60.0
25	H	11	1.0800	7	120.0	3	60.0
26	H	12	1.0800	7	120.0	3	180.0
27	H	12	1.0800	7	120.0	3	-60.0
28	H	12	1.0800	7	120.0	3	60.0
29	H	13	1.0800	8	120.0	4	180.0
30	H	13	1.0800	8	120.0	4	60.0
31	H	13	1.0800	8	120.0	4	-60.0
32	H	14	1.0800	8	120.0	4	180.0
33	H	14	1.0800	8	120.0	4	60.0
34	H	14	1.0800	8	120.0	4	-60.0

5C, ϕ = 60°:

1	C						
2	C	1	1.4624				
3	C	2	1.3883	1	120.0		
4	C	3	1.4941	2	120.0	1	180.0
5	C	4	1.3883	3	120.0	2	120.0
6	C	5	1.4623	4	120.0	3	180.0
7	C	3	1.4835	2	120.0	1	0.0
8	C	4	1.4835	5	120.0	6	0.0
9	H	1	1.0800	2	120.0	3	0.0

10	H	2	1.0800	3	120.0	1	180.0
11	C	7	1.5400	3	120.0	2	90.0
12	C	7	1.5400	3	120.0	2	-90.0
13	C	8	1.5400	4	120.0	5	90.0
14	C	8	1.5400	4	120.0	5	-90.0
15	H	5	1.0800	4	120.0	6	180.0
16	H	6	1.0800	5	120.0	4	0.0
17	C	1	1.3657	2	120.0	3	180.0
18	C	6	1.3657	5	120.0	4	180.0
19	H	17	1.0800	1	120.0	2	180.0
20	H	17	1.0800	1	120.0	2	0.0
21	H	18	1.0800	6	120.0	5	180.0
22	H	18	1.0800	6	120.0	5	0.0
23	H	11	1.0800	7	120.0	3	180.0
24	H	11	1.0800	7	120.0	3	-60.0
25	H	11	1.0800	7	120.0	3	60.0
26	H	12	1.0800	7	120.0	3	180.0
27	H	12	1.0800	7	120.0	3	-60.0
28	H	12	1.0800	7	120.0	3	60.0
29	H	13	1.0800	8	120.0	4	180.0
30	H	13	1.0800	8	120.0	4	60.0
31	H	13	1.0800	8	120.0	4	-60.0
32	H	14	1.0800	8	120.0	4	180.0
33	H	14	1.0800	8	120.0	4	60.0
34	H	14	1.0800	8	120.0	4	-60.0

5C, ϕ = 80°:

1	C						
2	C	1	1.4625				
3	C	2	1.3881	1	120.0		
4	C	3	1.4901	2	120.0	1	180.0
5	C	4	1.3881	3	120.0	2	100.0
6	C	5	1.4625	4	120.0	3	180.0
7	C	3	1.4836	2	120.0	1	0.0
8	C	4	1.4836	5	120.0	6	0.0
9	H	1	1.0800	2	120.0	3	0.0
10	H	2	1.0800	3	120.0	1	180.0
11	C	7	1.5400	3	120.0	2	90.0
12	C	7	1.5400	3	120.0	2	-90.0
13	C	8	1.5400	4	120.0	5	90.0
14	C	8	1.5400	4	120.0	5	-90.0
15	H	5	1.0800	4	120.0	6	180.0
16	H	6	1.0800	5	120.0	4	0.0
17	C	1	1.3657	2	120.0	3	180.0
18	C	6	1.3657	5	120.0	4	180.0
19	H	17	1.0800	1	120.0	2	180.0
20	H	17	1.0800	1	120.0	2	0.0
21	H	18	1.0800	6	120.0	5	180.0
22	H	18	1.0800	6	120.0	5	0.0
23	H	11	1.0800	7	120.0	3	180.0
24	H	11	1.0800	7	120.0	3	-60.0
25	H	11	1.0800	7	120.0	3	60.0
26	H	12	1.0800	7	120.0	3	180.0
27	H	12	1.0800	7	120.0	3	-60.0
28	H	12	1.0800	7	120.0	3	60.0
29	H	13	1.0800	8	120.0	4	180.0
30	H	13	1.0800	8	120.0	4	60.0
31	H	13	1.0800	8	120.0	4	-60.0
32	H	14	1.0800	8	120.0	4	180.0

33	H	14	1.0800	8	120.0	4	60.0
34	H	14	1.0800	8	120.0	4	-60.0

5C, ϕ = 100°:

1	C						
2	C	1	1.4624				
3	C	2	1.3881	1	120.0		
4	C	3	1.4927	2	120.0	1	180.0
5	C	4	1.3881	3	120.0	2	80.0
6	C	5	1.4624	4	120.0	3	180.0
7	C	3	1.4830	2	120.0	1	0.0
8	C	4	1.4830	5	120.0	6	0.0
9	H	1	1.0800	2	120.0	3	0.0
10	H	2	1.0800	3	120.0	1	180.0
11	C	7	1.5400	3	120.0	2	90.0
12	C	7	1.5400	3	120.0	2	-90.0
13	C	8	1.5400	4	120.0	5	90.0
14	C	8	1.5400	4	120.0	5	-90.0
15	H	5	1.0800	4	120.0	6	180.0
16	H	6	1.0800	5	120.0	4	0.0
17	C	1	1.3658	2	120.0	3	180.0
18	C	6	1.3658	5	120.0	4	180.0
19	H	17	1.0800	1	120.0	2	180.0
20	H	17	1.0800	1	120.0	2	0.0
21	H	18	1.0800	6	120.0	5	180.0
22	H	18	1.0800	6	120.0	5	0.0
23	H	11	1.0800	7	120.0	3	180.0
24	H	11	1.0800	7	120.0	3	-60.0
25	H	11	1.0800	7	120.0	3	60.0
26	H	12	1.0800	7	120.0	3	180.0
27	H	12	1.0800	7	120.0	3	-60.0
28	H	12	1.0800	7	120.0	3	60.0
29	H	13	1.0800	8	120.0	4	180.0
30	H	13	1.0800	8	120.0	4	60.0
31	H	13	1.0800	8	120.0	4	-60.0
32	H	14	1.0800	8	120.0	4	180.0
33	H	14	1.0800	8	120.0	4	60.0
34	H	14	1.0800	8	120.0	4	-60.0

5C, ϕ = 120°:

1	C						
2	C	1	1.4623				
3	C	2	1.3889	1	120.0		
4	C	3	1.4933	2	120.0	1	180.0
5	C	4	1.3889	3	120.0	2	60.0
6	C	5	1.4623	4	120.0	3	180.0
7	C	3	1.4807	2	120.0	1	0.0
8	C	4	1.4807	5	120.0	6	0.0
9	H	1	1.0800	2	120.0	3	0.0
10	H	2	1.0800	3	120.0	1	180.0
11	C	7	1.5400	3	120.0	2	90.0
12	C	7	1.5400	3	120.0	2	-90.0
13	C	8	1.5400	4	120.0	5	90.0
14	C	8	1.5400	4	120.0	5	-90.0
15	H	5	1.0800	4	120.0	6	180.0
16	H	6	1.0800	5	120.0	4	0.0
17	C	1	1.3658	2	120.0	3	180.0
18	C	6	1.3658	5	120.0	4	180.0
19	H	17	1.0800	1	120.0	2	180.0

20	H	17	1.0800	1	120.0	2	0.0
21	H	18	1.0800	6	120.0	5	180.0
22	H	18	1.0800	6	120.0	5	0.0
23	H	11	1.0800	7	120.0	3	180.0
24	H	11	1.0800	7	120.0	3	-60.0
25	H	11	1.0800	7	120.0	3	60.0
26	H	12	1.0800	7	120.0	3	180.0
27	H	12	1.0800	7	120.0	3	-60.0
28	H	12	1.0800	7	120.0	3	60.0
29	H	13	1.0800	8	120.0	4	180.0
30	H	13	1.0800	8	120.0	4	60.0
31	H	13	1.0800	8	120.0	4	-60.0
32	H	14	1.0800	8	120.0	4	180.0
33	H	14	1.0800	8	120.0	4	60.0
34	H	14	1.0800	8	120.0	4	-60.0

5D, $\phi = 0°$:

1	C						
2	C	1	1.4522				
3	C	2	1.4064	1	120.0		
4	C	3	1.6199	2	120.0	1	0.0
5	C	4	1.4064	3	120.0	2	180.0
6	C	5	1.4522	4	120.0	3	0.0
7	C	3	1.4777	2	120.0	1	180.0
8	C	4	1.4777	5	120.0	6	180.0
9	H	1	1.0800	2	120.0	3	0.0
10	H	2	1.0800	3	120.0	1	180.0
11	C	7	1.5400	3	120.0	2	90.0
12	C	7	1.5400	3	120.0	2	-90.0
13	C	8	1.5400	4	120.0	5	90.0
14	C	8	1.5400	4	120.0	5	-90.0
15	H	5	1.0800	4	120.0	6	180.0
16	H	6	1.0800	5	120.0	4	0.0
17	C	1	1.3665	2	120.0	3	180.0
18	C	6	1.3665	5	120.0	4	180.0
19	H	17	1.0800	1	120.0	2	180.0
20	H	17	1.0800	1	120.0	2	0.0
21	H	18	1.0800	6	120.0	5	180.0
22	H	18	1.0800	6	120.0	5	0.0
23	H	11	1.0800	7	120.0	3	180.0
24	H	11	1.0800	7	120.0	3	-60.0
25	H	11	1.0800	7	120.0	3	60.0
26	H	12	1.0800	7	120.0	3	180.0
27	H	12	1.0800	7	120.0	3	-60.0
28	H	12	1.0800	7	120.0	3	60.0
29	H	13	1.0800	8	120.0	4	180.0
30	H	13	1.0800	8	120.0	4	60.0
31	H	13	1.0800	8	120.0	4	-60.0
32	H	14	1.0800	8	120.0	4	180.0
33	H	14	1.0800	8	120.0	4	60.0
34	H	14	1.0800	8	120.0	4	-60.0

5D, $\phi = 20°$:

1	C						
2	C	1	1.4334				
3	C	2	1.4030	1	120.0		
4	C	3	1.7665	2	120.0	1	0.0
5	C	4	1.4030	3	120.0	2	160.0
6	C	5	1.4334	4	120.0	3	0.0
7	C	3	1.4809	2	120.0	1	180.0
8	C	4	1.4809	5	120.0	6	180.0
9	H	1	1.0800	2	120.0	3	0.0
10	H	2	1.0800	3	120.0	1	180.0
11	C	7	1.5400	3	120.0	2	90.0
12	C	7	1.5400	3	120.0	2	-90.0
13	C	8	1.5400	4	120.0	5	90.0
14	C	8	1.5400	4	120.0	5	-90.0
15	H	5	1.0800	4	120.0	6	180.0
16	H	6	1.0800	5	120.0	4	0.0
17	C	1	1.3685	2	120.0	3	180.0
18	C	6	1.3685	5	120.0	4	180.0
19	H	17	1.0800	1	120.0	2	180.0
20	H	17	1.0800	1	120.0	2	0.0
21	H	18	1.0800	6	120.0	5	180.0
22	H	18	1.0800	6	120.0	5	0.0

23	H	11	1.0800	7	120.0	3	180.0
24	H	11	1.0800	7	120.0	3	-60.0
25	H	11	1.0800	7	120.0	3	60.0
26	H	12	1.0800	7	120.0	3	180.0
27	H	12	1.0800	7	120.0	3	-60.0
28	H	12	1.0800	7	120.0	3	60.0
29	H	13	1.0800	8	120.0	4	180.0
30	H	13	1.0800	8	120.0	4	60.0
31	H	13	1.0800	8	120.0	4	-60.0
32	H	14	1.0800	8	120.0	4	180.0
33	H	14	1.0800	8	120.0	4	60.0
34	H	14	1.0800	8	120.0	4	-60.0

5D, ϕ = 40°:

1	C						
2	C	1	1.4203				
3	C	2	1.3846	1	120.0		
4	C	3	1.9667	2	120.0	1	0.0
5	C	4	1.3846	3	120.0	2	140.0
6	C	5	1.4203	4	120.0	3	0.0
7	C	3	1.5020	2	120.0	1	180.0
8	C	4	1.5020	5	120.0	6	180.0
9	H	1	1.0800	2	120.0	3	0.0
10	H	2	1.0800	3	120.0	1	180.0
11	C	7	1.5400	3	120.0	2	90.0
12	C	7	1.5400	3	120.0	2	-90.0
13	C	8	1.5400	4	120.0	5	90.0
14	C	8	1.5400	4	120.0	5	-90.0
15	H	5	1.0800	4	120.0	6	180.0
16	H	6	1.0800	5	120.0	4	0.0
17	C	1	1.3688	2	120.0	3	180.0
18	C	6	1.3688	5	120.0	4	180.0
19	H	17	1.0800	1	120.0	2	180.0
20	H	17	1.0800	1	120.0	2	0.0
21	H	18	1.0800	6	120.0	5	180.0
22	H	18	1.0800	6	120.0	5	0.0
23	H	11	1.0800	7	120.0	3	180.0
24	H	11	1.0800	7	120.0	3	-60.0
25	H	11	1.0800	7	120.0	3	60.0
26	H	12	1.0800	7	120.0	3	180.0
27	H	12	1.0800	7	120.0	3	-60.0
28	H	12	1.0800	7	120.0	3	60.0
29	H	13	1.0800	8	120.0	4	180.0
30	H	13	1.0800	8	120.0	4	60.0
31	H	13	1.0800	8	120.0	4	-60.0
32	H	14	1.0800	8	120.0	4	180.0
33	H	14	1.0800	8	120.0	4	60.0
34	H	14	1.0800	8	120.0	4	-60.0

5D, ϕ = 60°:

1	C						
2	C	1	1.4339				
3	C	2	1.3962	1	120.0		
4	C	3	1.6447	2	120.0	1	0.0
5	C	4	1.3962	3	120.0	2	120.0
6	C	5	1.4339	4	120.0	3	0.0
7	C	3	1.5345	2	120.0	1	180.0
8	C	4	1.45345	5	120.0	6	180.0
9	H	1	1.0800	2	120.0	3	0.0

10	H	2	1.0800	3	120.0	1	180.0
11	C	7	1.5400	3	120.0	2	90.0
12	C	7	1.5400	3	120.0	2	-90.0
13	C	8	1.5400	4	120.0	5	90.0
14	C	8	1.5400	4	120.0	5	-90.0
15	H	5	1.0800	4	120.0	6	180.0
16	H	6	1.0800	5	120.0	4	0.0
17	C	1	1.3687	2	120.0	3	180.0
18	C	6	1.3687	5	120.0	4	180.0
19	H	17	1.0800	1	120.0	2	180.0
20	H	17	1.0800	1	120.0	2	0.0
21	H	18	1.0800	6	120.0	5	180.0
22	H	18	1.0800	6	120.0	5	0.0
23	H	11	1.0800	7	120.0	3	180.0
24	H	11	1.0800	7	120.0	3	-60.0
25	H	11	1.0800	7	120.0	3	60.0
26	H	12	1.0800	7	120.0	3	180.0
27	H	12	1.0800	7	120.0	3	-60.0
28	H	12	1.0800	7	120.0	3	60.0
29	H	13	1.0800	8	120.0	4	180.0
30	H	13	1.0800	8	120.0	4	60.0
31	H	13	1.0800	8	120.0	4	-60.0
32	H	14	1.0800	8	120.0	4	180.0
33	H	14	1.0800	8	120.0	4	60.0
34	H	14	1.0800	8	120.0	4	-60.0

5D, ϕ = 80°:

1	C						
2	C	1	1.4576				
3	C	2	1.3939	1	120.0		
4	C	3	1.5168	2	120.0	1	0.0
5	C	4	1.3939	3	120.0	2	100.0
6	C	5	1.4576	4	120.0	3	0.0
7	C	3	1.4942	2	120.0	1	180.0
8	C	4	1.4942	5	120.0	6	180.0
9	H	1	1.0800	2	120.0	3	0.0
10	H	2	1.0800	3	120.0	1	180.0
11	C	7	1.5400	3	120.0	2	90.0
12	C	7	1.5400	3	120.0	2	-90.0
13	C	8	1.5400	4	120.0	5	90.0
14	C	8	1.5400	4	120.0	5	-90.0
15	H	5	1.0800	4	120.0	6	180.0
16	H	6	1.0800	5	120.0	4	0.0
17	C	1	1.3664	2	120.0	3	180.0
18	C	6	1.3664	5	120.0	4	180.0
19	H	17	1.0800	1	120.0	2	180.0
20	H	17	1.0800	1	120.0	2	0.0
21	H	18	1.0800	6	120.0	5	180.0
22	H	18	1.0800	6	120.0	5	0.0
23	H	11	1.0800	7	120.0	3	180.0
24	H	11	1.0800	7	120.0	3	-60.0
25	H	11	1.0800	7	120.0	3	60.0
26	H	12	1.0800	7	120.0	3	180.0
27	H	12	1.0800	7	120.0	3	-60.0
28	H	12	1.0800	7	120.0	3	60.0
29	H	13	1.0800	8	120.0	4	180.0
30	H	13	1.0800	8	120.0	4	60.0
31	H	13	1.0800	8	120.0	4	-60.0
32	H	14	1.0800	8	120.0	4	180.0

33	H	14	1.0800	8	120.0	4	60.0
34	H	14	1.0800	8	120.0	4	-60.0

5D, ϕ = 100°:

1	C						
2	C	1	1.4605				
3	C	2	1.3931	1	120.0		
4	C	3	1.5031	2	120.0	1	0.0
5	C	4	1.3931	3	120.0	2	80.0
6	C	5	1.4605	4	120.0	3	0.0
7	C	3	1.4810	2	120.0	1	180.0
8	C	4	1.4810	5	120.0	6	180.0
9	H	1	1.0800	2	120.0	3	0.0
10	H	2	1.0800	3	120.0	1	180.0
11	C	7	1.5400	3	120.0	2	90.0
12	C	7	1.5400	3	120.0	2	-90.0
13	C	8	1.5400	4	120.0	5	90.0
14	C	8	1.5400	4	120.0	5	-90.0
15	H	5	1.0800	4	120.0	6	180.0
16	H	6	1.0800	5	120.0	4	0.0
17	C	1	1.3660	2	120.0	3	180.0
18	C	6	1.3660	5	120.0	4	180.0
19	H	17	1.0800	1	120.0	2	180.0
20	H	17	1.0800	1	120.0	2	0.0
21	H	18	1.0800	6	120.0	5	180.0
22	H	18	1.0800	6	120.0	5	0.0
23	H	11	1.0800	7	120.0	3	180.0
24	H	11	1.0800	7	120.0	3	-60.0
25	H	11	1.0800	7	120.0	3	60.0
26	H	12	1.0800	7	120.0	3	180.0
27	H	12	1.0800	7	120.0	3	-60.0
28	H	12	1.0800	7	120.0	3	60.0
29	H	13	1.0800	8	120.0	4	180.0
30	H	13	1.0800	8	120.0	4	60.0
31	H	13	1.0800	8	120.0	4	-60.0
32	H	14	1.0800	8	120.0	4	180.0
33	H	14	1.0800	8	120.0	4	60.0
34	H	14	1.0800	8	120.0	4	-60.0

5D, ϕ = 120°:

1	C						
2	C	1	1.4639				
3	C	2	1.4012	1	120.0		
4	C	3	1.5097	2	120.0	1	0.0
5	C	4	1.4012	3	120.0	2	60.0
6	C	5	1.4639	4	120.0	3	0.0
7	C	3	1.4750	2	120.0	1	180.0
8	C	4	1.4750	5	120.0	6	180.0
9	H	1	1.0800	2	120.0	3	0.0
10	H	2	1.0800	3	120.0	1	180.0
11	C	7	1.5400	3	120.0	2	90.0
12	C	7	1.5400	3	120.0	2	-90.0
13	C	8	1.5400	4	120.0	5	90.0
14	C	8	1.5400	4	120.0	5	-90.0
15	H	5	1.0800	4	120.0	6	180.0
16	H	6	1.0800	5	120.0	4	0.0
17	C	1	1.3660	2	120.0	3	180.0
18	C	6	1.3660	5	120.0	4	180.0
19	H	17	1.0800	1	120.0	2	180.0

20	H	17	1.0800	1	120.0	2	0.0
21	H	18	1.0800	6	120.0	5	180.0
22	H	18	1.0800	6	120.0	5	0.0
23	H	11	1.0800	7	120.0	3	180.0
24	H	11	1.0800	7	120.0	3	-60.0
25	H	11	1.0800	7	120.0	3	60.0
26	H	12	1.0800	7	120.0	3	180.0
27	H	12	1.0800	7	120.0	3	-60.0
28	H	12	1.0800	7	120.0	3	60.0
29	H	13	1.0800	8	120.0	4	180.0
30	H	13	1.0800	8	120.0	4	60.0
31	H	13	1.0800	8	120.0	4	-60.0
32	H	14	1.0800	8	120.0	4	180.0
33	H	14	1.0800	8	120.0	4	60.0
34	H	14	1.0800	8	120.0	4	-60.0